

Quantitative characterization of site-occupancies in minerals

F. C. HAWTHORNE

*Department of Earth Sciences, University of Manitoba
Winnipeg, Manitoba, Canada R3T 2N2*

Abstract

Site-occupancies in minerals may be derived by a variety of experimental methods. The use of these methods is briefly reviewed here and particular attention is paid to the problems and limitations associated with the derivation of quantitative site-occupancies from experimental data. Diffraction methods are the most highly developed of these techniques, and for two species disordered over two or more sites can yield results the precision of which is dependent on the difference in the scattering powers of the atoms involved. Mössbauer spectroscopy is used primarily for Fe^{2+} and Fe^{3+} site-occupancy determinations. The precision of the results depends on the resolution of the spectrum; with decreasing resolution, parameter correlation becomes a problem in the spectrum refinement and precision is strongly decreased. Hydroxyl-band infrared spectroscopy has been used for site-occupancy determinations in OH-bearing minerals. However, this method is affected by clustering, and if it is to be used for quantitative site-occupancy determinations, either the absence of clustering has to be demonstrated or the method has to be further developed to allow for clustering. There has recently been considerable development in the use of electronic absorption spectroscopy for qualitative site-occupancy studies. Some quantitative work is now appearing, and there is considerable potential here for further development. Other methods used for qualitative or semi-quantitative work— γ -ray diffraction, X-ray photoelectron diffraction, X-ray and neutron diffraction powder profile-refinement, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy—have potential for fully quantitative work, but more development is required. Each method has its own area of particular usefulness, and these methods should be viewed as complementary rather than mutually exclusive.

Introduction

In the past twenty years, much information has become available concerning long-range atomic ordering in the crystal structures of minerals. This has been accompanied by investigations into the relationships between mineral composition, structural state, physical properties and ambient conditions of crystallization and/or equilibration. The experimental techniques by which such ordering is characterized have also undergone considerable development during this period. Conventional diffraction techniques have been refined, and are now capable of producing results of high precision. A number of spectroscopic techniques have been applied to the characterization of ordering in the past fifteen years, and some of these methods have been developed until they are now capable of giving quantitative results of high precision.

All of these methods have inherent limitations that pertain to the experimental method; most diffraction techniques require reasonably large, good quality crystals, many spectroscopic methods are not applicable to specific atomic species of interest, *etc.*; these limitations are quite well-known. When such techniques are used to

quantitatively determine ordering, there are other inherent problems associated with derivation of site-populations from the experimental results. It is these problems and the techniques that have been developed to deal with them that are the subject of this review. For the sake of completeness, most of the common methods of site-occupancy characterization will be briefly discussed. However, I will concentrate on those techniques that are in general use, because it is for these techniques that the problems associated with quantitative site-population derivation have been examined in detail. Experience suggests that similar problems will be encountered in other techniques when they are used extensively for site-population characterization.

Diffraction methods

Diffraction

The unit cell of a crystal contains atoms in various positions, and electro-magnetic radiation (with a wavelength comparable to lattice spacings) scattered from different atoms will have phase differences with respect to

each other. During Bragg diffraction, the amplitude F_{hkl} of the scattered wave is given by

$$F_{hkl} = \sum_{j=1}^n S_j \exp 2\pi i(hx_j + ky_j + lz_j) \exp(-B_j \sin^2 \theta/\lambda^2) \quad (1)$$

where S_j is the scattering factor at the j^{th} site in the cell, x_j are the positional coordinates of the j^{th} site, and B_j is the isotropic temperature factor, a function of the vibrational displacement of the atom(s) at the j^{th} site.

In a standard diffraction experiment, a large number of structure factors ($|F_{hkl}|$ values) are measured; this number is generally well in excess of the number of variable parameters of a crystal structure, and consequently these parameters may be determined from the structure factors. Examination of Equation (1) shows these parameters to be: (1) scattering factors at the n sites in the unit cell, (2) positional parameters for the n sites in the unit cell, (3) vibrational parameters at the n sites in the unit cell, together with a scale factor that relates the observed data to the calculations of Equation (1). In most structures, the presence of symmetry significantly reduces the number of variable parameters. More realistic models for the thermal vibration of atoms may be used, but this does not affect the subject of this paper. In general, the chemical composition of the crystal used in the diffraction experiment is known; thus the scattering factors are not generally considered as variable once the atoms have been correctly identified. The exception to this occurs when atoms are disordered over more than one crystallographically unique site, when the scattering factors at these sites are composite averages of all the atoms occupying these sites in the crystal. With the assumption that all atoms at a site have the same positional coordinates and thermal parameters, equation (1) may be modified to

$$F_{hkl} = \sum_{j=1}^n \left(\sum_{i=1}^m f_i a_{ij} \right) \exp 2\pi i(hx_j + ky_j + lz_j) \exp(-B_j \sin^2 \theta/\lambda^2) \quad (2)$$

where n is the number of occupied sites in the cell, a_{ij} are the site-occupancies of the j^{th} site by the i^{th} atom, and f_i is the scattering factor of the i^{th} atom. It is instructive to re-write Equation (1) in this way as it emphasizes that a single diffraction experiment can only determine the composite scattering from each site in the structure.

A vacancy may be considered as a scattering species with a scattering power of zero. Thus a site in a crystal can always be considered to be fully occupied by scattering species, even if it is not fully occupied by atoms. A single diffraction experiment gives the total scattering power S_j at each occupied site in a crystal structure:

$$S_j = \sum_i f_i a_{ij} \quad (3)$$

with a_{ij} subject to the constraint that the site be completely occupied by scattering species:

$$\sum_i a_{ij} = 1 \quad (4)$$

As we are primarily concerned with the derivation of site-occupancies, the form of the scattering factor f_i is of considerable interest. Most site-occupancy studies are generally carried out with X-rays or thermal neutrons. For X-rays, the scattering factor f is a complex function of $\sin \theta/\lambda$ (Fig. 1). For neutrons, the scattering is independent of $\sin \theta/\lambda$. For neutron scattering, equation (3) has solutions for $i = 2$ and $j = 1 \rightarrow \infty$ only; when $i > 2$ (three or more scattering species distributed over two or more sites), there is no general solution for a single neutron diffraction experiment. For X-ray diffraction, the relative decrease of scattering power with increasing $\sin \theta/\lambda$ differs slightly between scattering species. Thus equation (3) becomes a set of N equations, where N is the number of unique reflections recorded in the X-ray diffraction experiment. In principle, these equations can be solved for any number of scattering species (n) distributed over any number of sites (m). Hawthorne and Grundy (1977) used this idea to refine the occupancy of three scattering species over three sites in an amphibole; they obtained extremely large standard deviations using a full-matrix method, and concluded that it is impractical to derive site-occupancies of more than two scattering species distributed over two or more unique sites in a crystal.

Site-occupancy derivation

In the earliest studies concerned with site-occupancies, an overall temperature factor was applied to all atoms in the structure. On Fourier projections, site-occupancies were evaluated by electron counts or peak height values at the sites involved in the disorder (*e.g.*, Whittaker, 1949). An alternative method involved the calculation of R -factors for several possible alternative distributions of cations, generally for a subset of the structure factor data that was particularly sensitive to the site-occupancies adopted (Steinfink, 1962; Farrell *et al.*, 1963). Later, site-occupancies were determined by manual adjustment of the scattering factors such that the isotropic temperature factors at the sites involved were approximately equal (Ghose and Hellner, 1959; Ghose, 1961). There were two main drawbacks to this method. The solution was not a least-squares solution and least-squares standard deviations could not be assigned to the derived site-populations. Second, the assumption that the isotropic temperature factors at the sites involved in the atom disorder are equal is not necessarily valid. Burnham (1962) reviewed several factors upon which the magnitude of the isotropic temperature factors depend; such aspects as coordination number and degree of cation (or anion) substitutional disorder can significantly affect isotropic temperature factors.

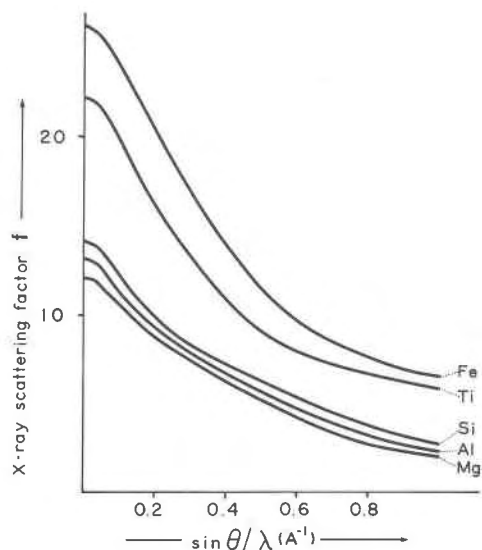


Fig. 1. X-ray scattering factors as a function of $\sin \theta/\lambda$ for some mineralogically important cations.

A more satisfactory solution would involve the direct determination of site-populations from least-squares refinement of diffraction data. This technique was proposed by Fischer (1963, 1968), who suggested two methods by which this could be done: (1) multiplying the scattering curve of an atom by a variable that is a refinable parameter in the least-squares procedure; (2) expressing the scattering power of the atoms occupying a site by the weighted sum of the individual scatterers; thus

$$f_m = a_{1m}f_1 + a_{2m}f_2 \quad (5a)$$

$$f_m = a_{1m}f_1 + (1 - a_{1m})f_2 \quad (5b)$$

Fischer (1966) used equation (5a) to determine the Fe–Mg site-occupancies in a cummingtonite originally refined by Ghose (1961). There were considerable correlation problems and the final solution had to be “normalized” to the known cell content. Burnham and Radoslovich (1963) used equation (5b) to successfully determine K–Na occupancies of the interlayer cation position in coexisting muscovite and paragonite.

In a refinement of the structure of grunerite, Finger (1969a) found that when the site-occupancies of the four M sites were refined, the sum of the refined site-occupancies did not agree with the bulk chemistry of the crystal calculated from a chemical analysis. This situation was also observed in other cases (e.g., Burnham *et al.*, 1971). In Equation (1), S_j and $\exp(-B_j \sin^2 \theta/\lambda^2)$ are of similar form. As F_{hkl} is the sum of products of these functions, they are highly correlated and the presence of $\sin \theta/\lambda$ dependent systematic error in the diffraction data induces systematic error in both S_j and B_j . This general problem was circumvented by constraining the sum of the site-

occupancies to be equal to the total site-group chemistry indicated by a chemical analysis (Finger, 1969b):

$$\sum_j b_j a_{ij} = C_i \quad (6)$$

where b_i is the multiplicity of the j^{th} site and C_i is the cell content of the i^{th} scattering species.

Finger (1969a) applied this method to site-occupancy refinement of grunerite, obtaining considerably reduced variable correlation and rapid convergence of the refinement. This constraint procedure was incorporated in the programs RFINE (Finger, 1969c) and RFINE4 (Finger and Prince, 1976) and has since been used in the refinement of site-occupancies in numerous minerals.

Constraints of the type indicated in Equations (4) and (6) may be thought of as rigid constraints, as the constrained parameters are forced to exactly obey the constraint equation. In the case of Equation (4), this is a valid assumption. For Equation (6), it is not as the cell content (C_i) of the i^{th} scattering species is generally an experimentally derived quantity and its exact value is not known. In addition, the diffraction data also contains information on the bulk composition of the crystal. Both these factors can be given weight in the refinement if the method of Waser (1963) is used to apply the constraints (Rollet, 1970). In this procedure, the constraints are treated in exactly the same way as the observational equations, and the suitably weighted squares of the residuals resulting from the constraint equations are incorporated in the minimization function

$$M = \sum_i w_i \Delta F_i^2 + \sum_k w_k \Delta p_k^2 \quad (7)$$

where ΔF_i is the difference of the observed and calculated structure factor for the i^{th} reflection, and Δp_k is the difference between the calculated constraint parameter c_n (calc.) and its observed value c_n (obs.). The weighting parameter w_k reflects the confidence with which the value of c_n (obs.) is known; thus w_k should be some inverse function of the standard deviation of c_n , with exact constraints having very high weight. However, the relationship between w_i and w_k (their relative magnitudes) is not all that clear. Where a bulk chemical constraint is only approximate, an overall charge-balance equation may be required to ensure that the overall formula remains electrostatically neutral.

Precision

The precision with which site-occupancies can be measured depends on the difference in scattering factors of the atoms involved. X-ray scattering factors are a function of atomic number. Thus it is easy to distinguish scatterers of disparate atomic number (such as Mg and Fe or Al and Fe) but ordering of atoms that are adjacent or near-neighbors in the periodic table (Al and Si, Fe and

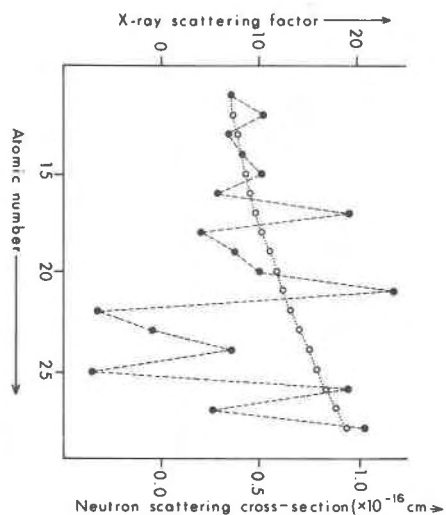


Fig. 2. A comparison of X-ray (o) and Neutron (●) scattering factors as a function of atomic number for some mineralogically important cations; X-ray scattering factors are calculated for $\sin \theta/\lambda = 0.30$.

Mn) cannot be reliably characterized in this fashion without resorting to special techniques. Using bulk chemical constraints of the form of Equation (6), Mg/Fe site-occupancies are routinely determined with assigned standard deviations of ~ 0.005 atoms. For Al/Si ordering, assigned standard deviations are generally > 0.1 and direct determination of site-occupancies by normal X-ray structure refinement is not practical. At high values of $\sin \theta/\lambda$, the relative difference in X-ray scattering factors between Al and Si increases, reaching $\sim 15\%$ at $\sin \theta/\lambda \sim 0.8$ – 0.9 . Fischer (1965) first proposed the determination Al/Si ordering by the refinement of high-angle X-ray data; Fischer and Zehme (1967) used this method for microcline, and Kosoi *et al.* (1974) used it for aluminous orthopyroxenes, quoting a (root?) mean square error of 0.04; both studies gave results that were in accord with the observed mean bond lengths. Conversely, Brown *et al.* (1974) were unsuccessful in attempts to refine Al/Si site-populations in sanidine using high-angle X-ray data (Phillips and Ribbe, 1972); they also noted large correlations (~ 0.87) between the occupancy parameters and the anisotropic temperature factor coefficients, suggesting that refinement of high-angle X-ray data is not an adequate method for characterization of Al/Si ordering in feldspars. Direct determination of Al/Si site-occupancies by refinement of high-angle data is probably now feasible using current state-of-the-art crystallographic techniques; however, the precision of such a determination is not known.

For neutron scattering, the scattering length of the elements increases gradually with increasing mass number, but is also subject to irregular fluctuations (Fig. 2). For most elements, the scattering length is positive, but

for a few (*e.g.*, H, Ti, Mn) it is negative. The significant differences in scattering lengths between some elements adjacent in the periodic table allow site-occupancy characterization that is not feasible by direct X-ray methods. Although the number of instances where this is possible is limited (Fig. 2), the fact the Ti and Mn have negative scattering lengths means that relative ordering of Fe–Ti and Fe–Mn can be very precisely characterized by neutron diffraction. This has not yet been exploited to any great extent, and thus the precision attainable on a routine basis is not yet known. The neutron scattering lengths of Al and Si differ by $\sim 20\%$. This difference has been used successfully by Brown *et al.* (1974), Prince *et al.* (1973) and other workers to successfully refine Al/Si site-occupancies to an adequate degree of precision ($\sigma \sim 0.02$ – 0.03) using constrained site-occupancy refinement techniques.

The standard deviations quoted above are routinely obtained in current site-occupancy refinements. However, these values may be somewhat misleading, as they are calculated with the assumption that the crystal composition is known exactly. In many cases, the precision of the bulk constraint calculated from the chemical analysis is much less than the precision of the site-occupancies determined. More reasonable standard deviations should be obtained using “soft” constraints, as in equation (7), but this has not yet been used extensively.

Disorder of three or more species

In order to obtain an exact solution to equation (3) for $i > 2$, more than one experiment is necessary. In general, for i species there must be $(i-1)$ values of S_j ; that is, $(i-1)$ diffraction experiments or a total of $(i-1)$ diffraction experiments plus externally derived site-occupancies. The value of such combined studies has been emphasized previously (Burnham *et al.*, 1971; Hawthorne and Grundy, 1977).

In a well-refined crystal structure, the mean bond lengths of coordination polyhedra are generally determined to quite high precision. Such mean bond lengths are related to the size of the cations and anions constituting the coordination polyhedron, and thus information on site-occupancy may be obtained. This situation is complicated by the fact that the factors controlling the variation of mean bond lengths in crystals are not completely understood despite considerable effort in this area (Shannon, 1975, 1976; Brown and Shannon, 1973; Baur, 1974, 1978). Thus simple comparison of ionic radii sums cannot be expected to yield accurate answers except in the more extreme and/or fortuitous cases. However, many studies have shown that in groups of isomorphous structures, the mean bond lengths of individual coordination polyhedra may be related fairly precisely to the mean ionic radii of the constituent cations (Novak and Gibbs, 1970; Brown, 1978; Cameron and Papike, 1980; Hawthorne, 1981a). This is presumably the result of the fact that the ligan-

and local environment of the coordination polyhedron remain reasonably constant across the series of structures, and the polyhedron responds linearly to the variations in cation size without any other factors affecting the stereochemistry. Where such relationships are well-characterized, they can be used to derive site-occupancies or contribute to site-assignments in structure refinements.

For $i > 2$, equation (3) may have ranges of parameter values that lead to physically impossible solutions (*i.e.*, negative site-occupancies), thereby placing limits on possible site-occupancies. In most cases, these limits will be so wide as to be of little value. However, an advantageous combination of positive and negative scattering species in neutron diffraction can lead to a limited range of real solutions that can provide useful information. As an example of this, consider the site-occupancy refinement of potassian oxy-kaersutite (Kitamura *et al.*, 1975). When the observed neutron scattering densities at the three octahedrally coordinated M sites are considered together with the unit cell contents from the chemical analysis, allowable solutions to the site-occupancy equations occur for M(1) Ti site-occupancies between ~ 0.25 and ~ 0.29 ; as this accounts for nearly 90% of the Ti in the unit cell, an adequate answer to the question of Ti distribution in oxy-kaersutite was derived from the experiment even though an exact solution was not obtained.

Specific radiation diffraction

The essential feature of these methods, as developed by Duncan *et al.* (1973), is to perturb normal Bragg scattering by a competing mechanism that is related to the presence of the cation (or anion) of interest in the mineral. The difference between the scattering in the normal and perturbed conditions consists predominantly of information concerning the site-distribution of the atom of interest. Methods of this type have not been used to any great extent, but they have the potential to characterize atoms that cannot easily be examined by other methods due to interference from other atoms in the structure.

Duncan *et al.* (1975) and Johnston and Duncan (1975) used anomalous X-ray scattering to derive the site-distributions of Fe^{2+} and Mn^{3+} in cordierite and tourmaline respectively. Here, a specific type of atom is induced to scatter anomalously by using X-rays of a wavelength close to its absorption edge. The results are compared with those of a normal scattering experiment, in principle isolating the anomalous scattering contribution and measuring the distribution of the anomalous scatterer. The method was demonstrated using both powder diffraction of $\text{FeK}\alpha$ and $\text{CuK}\alpha$ radiation, and single-crystal ($10 \times 10 \times 1$ mm plate) diffraction of white X-radiation using energy dispersive detection. Only three or four reflections were measured in each case; a much larger data set is preferable, low counting times notwithstanding. As suggested by Whittaker (1975), the use of synchrotron radiation would speed up measurement time and allow

the use of smaller specimens with the energy dispersive method.

Duncan *et al.* (1973) suggest using γ -ray diffraction with a moving γ -ray source. Under these conditions, any Mössbauer sensitive isotopes present will also show nuclear scattering when the source is moving at the resonance velocity. Comparison of the diffraction on and off resonance gives information concerning the phase of the contribution from the Mössbauer sensitive atom; thus ordering may be characterized. No details of such a determination are yet available.

X-ray photoelectron spectroscopy is a technique of considerable potential with regard to the characterization of order/disorder in minerals. At present, the low resolution of the technique precludes its use on a quantitative level, but future improvements in both intensity and resolution should promote its use in this area. A review of the application of this technique to geology is given by Bancroft *et al.* (1979). Photoelectrons generated below the surface of a single-crystal may be diffracted before they reach the surface of the crystal. The resultant ejected electron flux shows directional anisotropy that is a function of the structure of the sample crystal. Adams *et al.* (1978) have used this technique of *X-ray photoelectron diffraction* to characterize cation ordering in micas. The potential of this technique is considerable, but much development is required before the results are fully quantitative.

Powder diffraction methods

The discussion given above has centered on single-crystal diffraction. Many minerals, both natural and synthetic, do not occur in crystals suitable for single-crystal diffraction experiments. Quantitative information on ordering can be derived by powder diffraction provided the structure is not too complex. In a powder diffraction pattern, reflections generally overlap and thus individual intensities cannot be measured directly. However, much of the information in these intensities is still present in the powder pattern. This may be extracted and used for structure refinement using the profile-fitting refinement procedure of Rietveld (1969). Although primarily used for powder neutron diffraction, the method has also been used for site-occupancy characterization in powder X-ray diffraction (Nord, 1977; Nord and Stefanidis, 1980).

Mössbauer spectroscopy

Mössbauer resonance

The Mössbauer effect is the recoil-free emission and absorption of γ -rays by a specific atomic nucleus. The emission of a γ -ray during a nuclear transition normally causes a recoil of the emitting atom; this recoil energy dissipates by transfer to the phonon spectrum of the structure. As the phonon spectrum is quantized, this transfer must occur in integral multiples of the phonon

energy and the probability exists that no energy is transferred. The effective line-width of the zero-phonon (recoil-free) process is that of the γ -ray; this is extremely small (Wertheim, 1964, Chap. 4, Fig.1) in relation to the characteristic energies of interaction between the nucleus and its surrounding electrons. If the zero-phonon γ -ray encounters another nucleus, its energy may be absorbed by raising that nucleus to an excited state, provided the transition energies of the emission and absorption events are equal to within the line-width of the γ -ray. As the line-width of the γ -ray is much smaller than the characteristic interaction energies between nuclei and electrons, a change in structural environment is generally sufficient to bring the two nuclei out of resonance. However, the energy of the γ -ray may be modulated by applying a doppler shift to bring the system into resonance. In this way, nuclear transition energies may be compared in different environments.

A change in the s -electron density at the nucleus of an atom will result in a shift in the nuclear energy levels. Where such a variation occurs between emitter and absorber, the processes are separated in the energy spectrum by an amount known as the *Isomer Shift* (IS) or *Chemical Shift* (CS). This quantity is thus a measure of the relative s -electron density at the nucleus. Two factors are principally responsible for variations in isomer shift. Screening of s -electrons from the nucleus by valence electrons is strongly affected by valence state and degree of covalent bonding. Thus isomer shift may be used to characterize valence state and coordination number. If the nucleus does not have a uniform charge density, a quadrupole moment arises which can interact with the electric field gradient (EFG) at the nucleus to lift the degeneracy of the nuclear states. The splitting of the nuclear energy levels gives rise to a series of possible transitions between the ground and excited states of the nucleus, the number of which depends on the nuclear spin quantum number. For ^{57}Fe ($I = 1/2$) in paramagnetic materials, the ground state is not split and the first excited state ($I = 3/2$) is split into two levels; the two allowable transitions give rise to a doublet in the energy spectrum; the separation of the two components is known as the *Quadrupole Splitting* (QS) and is thus a measure of the EFG at the nucleus. Principal factors affecting the EFG at the nucleus are the non-spherical electron distribution in the atom itself, a function of valence state, and the non-spherical component of the crystal field. Thus quadrupole splitting may be used to characterize valence state and variations in structural environment.

Site-occupancy derivation

There are thirty or so isotopes that are sensitive to the Mössbauer effect. There have been some studies of Sb and Sn in minerals (Stevens and MacIntosh, 1977; Baker and Stevens, 1977) but virtually all quantitative site-population studies have involved ^{57}Fe . Early studies of iron in minerals (Pollak *et al.*, 1962; de Coster *et al.*, 1963)

were reconnaissance in nature. Gibb and Greenwood (1965) correctly assigned the spectrum of cummingtonite by a qualitative consideration of site-populations. The introduction of least-squares refinement techniques to spectrum fitting led to quantitative and more extensive studies of iron site-populations in silicate minerals (Bancroft *et al.*, 1966, 1967a,b; Evans *et al.*, 1967, Ghose and Hafner, 1967; Virgo and Hafner, 1968, 1969).

Bancroft (1967, 1970) and Bancroft *et al.* (1967a) have considered the assumptions inherent in using the Mössbauer effect for site-population characterization of iron in silicates when two distinct quadrupole split doublets occur in the spectrum. We may generalize this to r quadrupole split doublets in the spectrum. The area under a peak is given by (Bancroft *et al.*, 1967a)

$$A_i = \frac{\pi}{2} f_i f_e \sigma_0 \tau_i G(n_i, f_i, \sigma_0) n_i \quad (8)$$

where f_i is the recoil-free fraction of the absorber at the site giving rise to the peak i , f_e is the recoil-free fraction of the emitter, σ_0 is the maximum resonant absorption cross-section (= peak height per absorbing atom), τ_i is the half-width of the peak (peak width at half-height), $G(n_i, f_i, \sigma_0)$ is the saturation correction, and n_i is the number of atoms per formula unit at the site giving rise to the peak i . Expressing the area of the j^{th} peak as a function of the total absorption

$$A_j / \sum_{i=1}^r A_i = n_j / \sum_{i=1}^r C_i n_i \quad (9)$$

where

$$C_i = \frac{f_i}{f_j} \frac{\tau_i}{\tau_j} \frac{G_i(n_i, f_i, \sigma_0)}{G_j(n_j, f_j, \sigma_0)}$$

In most studies, C_i is assumed to be unity. Considering the individual terms in the above expression for C_i , this generally seems to be a reasonable assumption, but has never been proven to be correct in a solid solution series. Saturation corrections approach unity for thin absorbers, and small deviations from this value should be self-cancelling providing that the n_i values are not radically different from each other (Bancroft, 1973). This is not the case when measureable saturation does occur; this situation can be corrected by running at lower absorber concentrations. Extensive experimental evidence has confirmed that half-widths of *single-peaks* are approximately equal. The recoil-free fractions at energetically similar sites should be equal. In principle, the recoil-free fractions can be determined, but this has rarely been done. Some studies have derived C values different from unity but such results have often been somewhat controversial.

An experimental Mössbauer spectrum is shown in Figure 3. Each data point represents the number of counts recorded over that particular source velocity

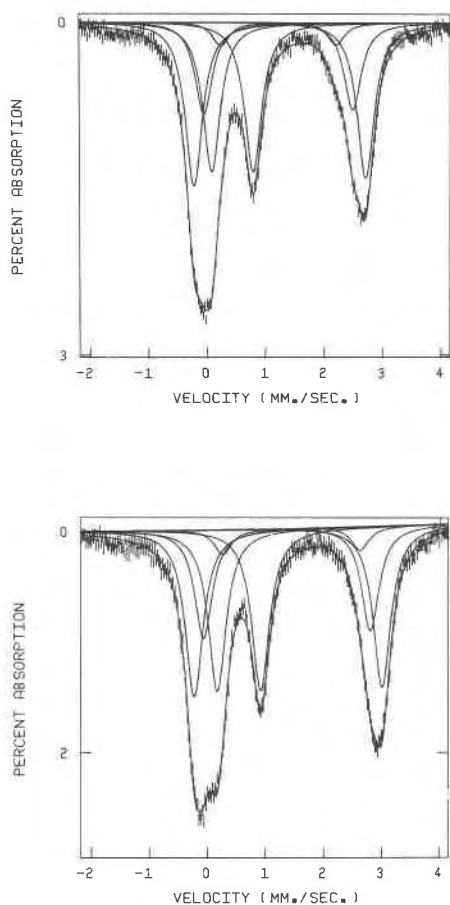


Fig. 3. The Mössbauer spectrum of potassian ferri-taramite.

interval, and the length of the vertical dash represents two standard deviations based on counting statistics. The counts at the margins of the spectrum represent the background counts and are approximately constant; the average background value is termed the off-resonance count. Towards the center of the spectrum, the counts decrease; this is due to the resonant absorption of γ -rays of this specific energy by the sample. The ideal shape of a single absorption peak (line) in a Mössbauer spectrum is Lorentzian. Thus the observed spectrum consists of a series of Lorentzian peaks, the number and characteristics of which are a function of the crystal structure of the sample. Unfolding the observed envelope into its component Lorentzian peaks is done using least-squares refinement techniques. The intensity of the transmitted beam y as a function of its energy x for a spectrum containing l lines may be expressed as

$$y = b - \sum_{i=1}^l \frac{b - y(0)_i}{1 + 4(x - x(0)_i)^2/a_i^2} \quad (10)$$

where $x(0)_i$ is the resonant velocity of the i^{th} peak, $y(0)_i$ is the beam intensity at the resonant velocity of the i^{th} peak,

a_i is the i^{th} peak half-width (full width at half peak height), and b is the background intensity. The area of the i^{th} peak may be written as

$$A_i = \pi a_i (b - y(0)_i) / 2 \quad (11)$$

Slight sinusoidal and linear deviations occur in the background intensity due to source movement and instrumental drift; b is modified in the above intensity equation to account for these features. Least-squares refinement procedure minimizes R_0 , the weighted sum of the squares of the residuals for each data point (spectrum channel):

$$R_0 = \sum_{r=1}^m w_r [y_r^0 - y_r^c]^2 \quad (12)$$

where w_r is the weight of the r^{th} observations (usually assigned from counting statistics), y_r^0 is the observed beam intensity at the r^{th} channel, and y_r^c is the calculated beam intensity at the r^{th} channel (calculated using the least-squares parameter estimates). Law (1973) has considered the case when there is no systematic error in the data or the model. In this case, an ideal residual defined as

$$R_1 = \sum_{r=1}^m w_r [y_r^0 - y_r^l]^2 \quad (13)$$

where y_r^l is the calculated beam intensity at the r^{th} channel (calculated using the correct parameter values), would be non-zero on account of random error in the data. R_1 follows the chi-squared distribution; if a set of fitted parameters is a valid approximation to the correct set of values, then R_0 is a value from this distribution (Law, 1973). To test the hypothesis that the least-squares parameter estimates are a valid approximation to the correct values, the percentage points of the chi-squared distribution are used to assess the probability that R_1 would exceed R_0 . When refining spectrum parameters, a decrease in R_0 is generally associated with an improvement in the model, until an acceptable fit occurs when R_0 lies between the 99% and 1% points of the chi-squared distribution. Within these limits, statistical tests cannot discriminate between alternate models (Law, 1973). Given two statistically acceptable solutions to the spectrum-fitting procedure, the simpler solution is to be preferred on statistical grounds alone. However, if additional information is available from another technique that indicates that the more complex solution is correct, then the more complex solution is to be preferred. In this case, we constrain our solution on the basis of external information, and the simpler solution is rejected not on statistical grounds, but because it does not conform with these external constraints.

Statistical tests are used as a measure of comparison between alternate models, with the residual as a measure of the agreement between the observed data and a

corresponding set of calculated values derived from the least-squares solution. Statistical acceptability and a low residual are no guarantee that the derived model is correct; they merely indicate that the derived model adequately (but not exclusively) explains the observed data. The most obvious examples of this are the Mössbauer spectra of the amphiboles of the magnesiocummingtonite-grunerite series (Bancroft *et al.*, 1967a; Hafner and Ghose, 1971). The C2/m amphibole structure indicates that the correct (ideal) spectrum model should consist of four quadrupole-split Fe^{2+} doublets. However, statistically acceptable fits are obtained for two quadrupole-split Fe^{2+} doublets. Doublet intensity (Bancroft *et al.*, 1967a; Hafner and Ghose, 1971; Ghose and Weidner, 1972) and local stereochemistry (Hawthorne, 1981b) show that three of the four doublets overlap almost perfectly in the spectra and have very similar IS and QS values. The correct (ideal) four-doublet model cannot be resolved, as the spectrum does not contain sufficient information for this to be done. This is not to say that useful information cannot be derived from the two-peak solution in this particular case; however, it does illustrate that statistical acceptability and correctness are not necessarily concomitant.

For most problems of interest in mineralogy, Mössbauer spectra consist of a complex overlap of peaks that reflect differential occupancy of more than one crystallographic site in the mineral structure. In such cases, the precision with which the parameters of interest can be determined is strongly a function of the degree of overlap of the constituent peaks. This has been investigated by Dollase (1975) for the case of two overlapped peaks using simulated spectra. Several interesting features emerged from this work. First, for equal area and equal width Lorentzian peaks, separate maxima in the envelope occur for peak separations greater than $1/\sqrt{3}$ (~0.6) peak width. Second, the uncertainty associated with the derived peak area is a function of the peak separation and the peak-to-background ratio. Because Fe^{3+} shows much less variation than Fe^{2+} in quadrupole splitting values for most minerals, complex Fe^{3+} spectra generally show far greater overlap than comparably complex Fe^{2+} spectra. Consequently, Fe^{3+} site-occupancies are usually far less precisely determined than Fe^{2+} site-occupancies.

The problems associated with peak overlap and the corresponding correlation problems in the least-squares fitting procedure may be alleviated somewhat by incorporating into the model additional information that is external to the spectral data itself. There are two types of constraints that are widely used:

(1) *Width constraints*: Mössbauer spectral examination of many end-member compounds suggests that the peak widths corresponding to Fe^{2+} in various sites are equal in a specified sample. Thus in the spectrum refinement procedure, the width of all the peaks can be constrained to be equal, with a considerable improvement in both the convergence rate and standard deviations.

This is a commonly used constraint; however, it may not always be valid. In a solid solution, variation in the local environment of a site can cause peak broadening (substitutional broadening); if the amount of variation differs among the different unique sites in a structure, differential substitutional broadening may result, leading to different half-widths for different Fe^{2+} doublets. For Fe^{3+} in very dilute concentrations, relaxation broadening (Blume, 1966; Wignall, 1966) may produce peak-width asymmetry, as appears to be the case in clinzoisites (Dollase, 1973). Despite these cases cited here, for complex mixed-valence minerals, a general equal peak-width constraint may be advisable unless there is strong evidence to suggest otherwise; there is a danger that a single Fe^{3+} doublet with an unconstrained peak-width may pick up all sorts of minor contributions that arise from minor errors in several Fe^{2+} doublets and end up considerably distorted from its correct configuration.

(2) *Area constraints*: Experimental evidence suggests that the individual peaks of a quadrupole-split doublet should have approximately equal intensity (Bancroft *et al.*, 1967b). This is another very powerful constraint that is frequently used in spectral refinement. This constraint may not be strictly correct as preferred orientation in a sample can give rise to intensity asymmetry in quadrupole-split doublets (see, for example, the single-crystal spectra given by Duncan and Johnston, 1974, and Goldman *et al.*, 1977). Fortunately, mixing and grinding the sample with an inert equidimensional filler such as sugar satisfactorily removes preferred orientation. Generally an asymmetry of a few percent is present in most spectra, but is generally not sufficient to interfere with the spectrum fitting and useful operation of equal-intensity constraints. Such residual asymmetry could be crudely handled by including an overall asymmetry parameter in the refinement process, but such a procedure is not generally used.

In complex, poorly-resolved spectra, such as that shown in Figure 3, the final solution is only as good as the constraints which were used in the fitting procedure. If the constraints are true, then the fitted parameters are valid; however, if the constraints are wrong (or inappropriate) then the solution will be wrong. As emphasized above, the selection of constraints requires careful consideration of the problem at hand, and the constraints finally used may represent a compromise between the "ideal" constraints and the constraints that give the most realistic solution. These width and area constraints are rigid constraints as applied in normal spectrum fitting procedures. These constraints are not exact (width and area constraints, even if ideally exact, are perturbed by substitutional broadening and residual orientation and, in addition, the spectrum contains information on relative peak widths and relative areas of QS doublet components). Consequently they should be used as "soft" constraints rather than hard constraints, as discussed in the section on diffraction.

Precision

Least-squares refinement is a widely used method in science. The reason for this is that once convergence has been attained, some kind of precision (a standard deviation) can easily be assigned to the variable parameters of the model. However, some Mössbauer studies in the literature do not report standard deviations for their assigned site-population. These values are not useful without some estimation (a minimum estimation in the case of least-squares modelling) of their precision. The site-occupancy (x_j) of the Mössbauer-sensitive atom at the j^{th} site may be written as

$$x_j = R_j \frac{X^t}{m_j} \quad (14)$$

where R_j is the relative area of the doublet assigned to x_j , X^t is the total amount of Mössbauer sensitive species per unit cell, and m_j is the rank of the equipoint of the j^{th} site (the number of j^{th} sites in the unit cell).

Thus the standard deviation of the site-population is made up of contributions from R_j and X^t . Generally the standard deviation associated with X^t is neglected (although there is no reason why this should be done), and the standard deviation of the site-population is the scaled standard deviation of the area ratio R_j . In order that the calculated standard deviations be correctly calculated, all variable parameters must have been varied in the last least-squares cycle and the full variance-covariance matrix must be used in the error propagation calculation for the area ratio.

Standard deviations derived from non-linear least-squares refinement must be treated with caution. If the estimated standard deviations are small enough that the functions are linear over a range of several standard deviations, then the normal methods of testing linear hypotheses can be applied; this is hopefully the general case in most uses of least-squares refinement. However, if there are departures from linearity in this range, as is to be expected if high correlations give rise to large standard deviations, then variance-ratio tests are no longer exact. This is presumably the origin of the "imprecisely determined" standard deviations in the study of Dollase (1975), and this effect should be borne in mind when assessing the significance of site-populations derived from spectra in which high correlations are encountered.

Single-crystal Mössbauer method

For a single-crystal absorber, the area ratio of the peaks of a quadrupole-split doublet is a function of the angle the incoming γ -ray beam makes with the electric field gradient at the Mössbauer nucleus. If a Mössbauer-sensitive species occupies more than one crystallographically unique site in a structure, the response of atoms at each site to changing incidence angle of the γ -ray beam will be different, provided significant differences in the EFG occur at each of these sites. Thus site-occupancies

can be derived from the variation of the upper and lower velocity area ratios with γ -ray incidence angle, without having to resolve the individual quadrupole-split peaks. Duncan and Johnston (1973) have used this method to derive site-occupancies in olivine, where great difficulty is encountered in resolving and assigning individual quadrupole-split doublets in the powder Mössbauer spectrum. Duncan and Johnston (1974) used this method to assign site-occupancies in cordierite, but their results are questioned by Goldman *et al.* (1977). This method seems to have potential for poorly resolved but fairly simple spectra; however, for more complex spectra, the solution is probably not very well defined.

Vibrational spectroscopy

Vibrational spectroscopy involves the interaction between electro-magnetic radiation and the vibrational modes of a crystal. A vibrational mode in a crystal will absorb electromagnetic radiation if the frequencies of the vibration and the radiation are coincident and if the excited vibration results in a change in the dipole moment of the crystal; this gives rise to *infrared absorption spectroscopy*. Electromagnetic radiation may be elastically scattered by a crystal (Rayleigh scattering). Scattering may also occur inelastically. In this case, the scattering episode is accompanied by a vibrational transition in the crystal, where energy is absorbed from or imparted to the scattered radiation; this is the Raman effect and gives rise to *Raman spectroscopy*.

Both methods have found considerable application for order-disorder phenomena in solids, and comprehensive reviews are given by White (1967, 1974) and White and Keramidis (1972). These authors also give a classification of the different types of ordering that can occur, derivative from a parent structure. Most types of ordering considered involve a change in cell size and/or symmetry. The principal applications of vibrational spectroscopy involve the characterization of such ordering by factor group analysis of the vibrational spectra (White and DeAngelis, 1967; DeAngelis *et al.*, 1971). Such an approach is not applicable to many problems of mineralogical interest where relative cation ordering at non-equivalent sites does not affect the factor group symmetry of the crystal. However, where a particular vibrational band can be associated with the vibration at a specific site in a crystal, variation in the cation type occupying that site can be correlated with a shift in frequency of the associated spectral band. Most work in this area has involved infrared spectroscopy. The Raman effect requires exact translational symmetry over several unit cells in order to produce a sharp spectrum (White, 1975). Perturbation of this symmetry by order-disorder causes rapid peak broadening and loss of detail in the Raman spectrum, suggesting that Raman spectroscopy will be of limited application to this type of order-disorder. Experimental evidence to this effect can be seen by comparing the

Raman spectra for actinolite (White, 1975) and tremolite (Blaħa and Rosasco, 1978).

A random solid solution should exhibit the vibrational bands characteristic of its end-members, with a linear shift in frequency with composition. This type of behavior has often been observed for mineral series, and is generally accompanied by peak-broadening in the central regions of the series. Such peak-broadening in the infrared spectra is a useful qualitative indicator of disorder in series that show order-disorder over more than one unique site in a crystal (Martin, 1970; Estep *et al.*, 1971; Farmer and Velde, 1973). Burns and Huggins (1972) and Kovach *et al.* (1975) noted non-linear variation with composition for some bands in the infrared spectra of olivines and pyroxenes. They suggested that this was due to significant cation ordering over the octahedral sites in the structures of these minerals. Huggins (1973) further developed this idea to quantitatively derive site-populations in manganese olivines; however, no comparative studies of this method have yet been made. Perhaps the most precise method of characterization involves the correlation of band position with order/disorder parameter for a fixed mineral composition.

The hydroxyl stretching region

A fragment in many common hydroxyl-bearing minerals is the edge-sharing octahedral trimer $[M_3\phi_{12}(OH)]$ (ϕ = unspecified anion); this is embedded in the structures of the humites, the amphiboles, the micas, talcs and chlorites.

The fundamental band of the O–H stretching vibration occurs from 1500–3800 cm^{-1} . The exact position of this band in the infrared region is a function of the strengths of the hydrogen–oxygen bond; strong bonds are associated with higher frequencies, the lower end of the range being characteristic of symmetrical hydrogen bonds (Hamilton and Ibers, 1968). In the spectra of minerals containing this cluster, the fundamental band generally occurs from 3600–3700 cm^{-1} , indicative of a strong hydroxyl bond and little or no hydrogen bonding. Minerals containing a completely ordered arrangement of cations in this cluster show a single sharp hydroxyl stretching band in this region. However, the principal band in minerals of intermediate composition shows considerable fine structure. Bassett (1960) was first to make the connection between fine-structure in the OH stretching region and the cation arrangement in the coordinating sites when he interpreted such structure in the spectra of biotites as being due to vacancies in the octahedral layer. Vedder (1964) confirmed this association between OH fine-structure and cation configuration in the octahedral layer of phlogopites in a very detailed study. Strens (1966) and Burns and Strens (1966) interpreted the fine-structure bands in amphiboles in terms of cation disorder over the octahedrally-coordinated sites in the structure, and used the relative intensity of the various bands to derive the frequency of occurrence of the different possible combinations of

cations and the cation ordering over the non-equivalent sites in the structure. Similar quantitative interpretations were subsequently made for the micas (Wilkins, 1968) and the talcs (Wilkins and Ito, 1967), and the method has been used in systematic site-occupancy studies (Burns and Prentice, 1968; Burns and Greaves, 1971).

Frequency shift

Strens (1974) has shown that the frequency shift of the individual bands in the fine-structure is a function of the electronegativity of the bonded cations. This suggests that the frequency shift is related to the relative covalency of the cation-hydroxyl bond. The resolution of these bands in the hydroxyl spectrum is a function of both band width and frequency shift. The intrinsic width of the bands in end-member ordered structures is $\sim 5 \text{ cm}^{-1}$, which is usually broadened to $\sim 6 \text{ cm}^{-1}$ by instrumental and minor substitutional effects. The frequency shift is generally considerably greater than the band width; thus the principal resolution problems arise from accidental overlap of configurations having similar frequency shifts. One complicating factor is the presence of cation substitutions at sites not coordinated to the hydroxyl and their possible effect on the frequency of the bands. This is best documented for the amphiboles, in which alkali cations entering the A-site increase the principal OH stretching frequency considerably ($+24 \text{ cm}^{-1}$ in riebeckite (Strens, 1974); $30\text{--}40 \text{ cm}^{-1}$ for hastingsite and pargasite (Semet, 1973); 56 cm^{-1} and 62 cm^{-1} respectively for richterite and potassium-richterite (Rowbotham and Farmer, 1973)). This suggests that the chemically more complex minerals will give so many bands that the spectra will become too complex to be resolved. Where cation substitutions in sites not coordinated to OH do not have such a great effect on the stretching frequency, the peaks may merely be broadened rather than split into different peaks. Again, this will cause problems as such substitutional broadening will decrease the resolution of the spectrum and lead to less well-defined band intensities.

The derivation of band intensities

The derivation of band intensities from a measured spectrum is a difficult problem even in the simplest of cases, and some of the difficulties involved have been discussed by Strens (1974). Three main methods have been used: (1) graphical resolution, (2) use of a curve resolver, and (3) least-squares refinement.

Several problems are common to all three methods. First, it is usually necessary to apply substantial baseline corrections to the observed spectrum (see Burns and Greaves, 1971, Figs. 1 and 2). Most studies do not mention how this is done, but Strens (1974) indicates that the baseline is usually drawn in freehand by the experimenter. Obviously such a subjective procedure cannot be considered satisfactory. Similar problems in the fitting of Mössbauer spectra are handled by a baseline refinement technique. Such an approach is also necessary for the

infrared technique if the method is to give objective results. The second factor involved in each of the resolution methods is the form of the band shape. In principle, vibrational bands are Lorentzian but line-broadening usually results in a band shape that approximates a skewed Gaussian (Strens, 1974). If a normal Gaussian is used, this may give rise to spurious weak bands in the fitted spectra.

The first two methods outlined above are highly subjective; however, both are useful for deriving starting parameters for numerical fitting procedures. The latter will usually involve the least-squares technique, possibly with the use of linear constraints, with the major advantage that standard deviations can be derived.

Other considerations

The derivation of site-occupancies from band intensities assumes that the band intensity for a specific configuration is related to the frequency of occurrence of that configuration in the same way that all other bands are related to their corresponding configurations. Thus the transition moment of the OH vibration should be independent of the type of configuration. Work on micas (Rouxhet, 1970) suggests that this is not so, and the limited amount of work done on amphiboles in this regard is also apparently in accord with this conclusion (Strens, 1974). The occurrence of weak hydrogen bonding may significantly affect the transition moment of the OH band, whether or not the strength of the hydrogen bonding is related to the cation configuration at the coordinating octahedral sites.

In many structures, the hydroxyl position may be occupied by F, Cl (and O^{2-}) in addition to OH. In order to apply this method, it is necessary to assume that there is random mixing of OH, F, Cl anions with no segregation at specific cation configurations. Unfortunately, this does not appear to be the case, as Fe^{2+} tends to avoid F-coordinated sites (Rosenburg and Foit, 1977).

Hydroxyl infrared spectra have found most use in site-occupancy studies of Mg/ Fe^{2+} and Mg/ $Fe^{2+}/Fe^{3+}/Al$ ordering over the M(1), M(2) and M(3) sites in amphiboles. It is instructive to consider the specific case of Mg/ Fe^{2+} ordering in $C2/m$ amphiboles, following the work of Law (1976). When Fe^{2+} and Mg only are present at the octahedrally coordinated sites coordinating a single hydroxyl-2M(1) + M(3)-, the OH absorption band consists of four component peaks:

- A $2M(1) + M(3) = 3Mg$
- B $2M(1) + M(3) = 2Mg + Fe^{2+} \text{ } \square (\equiv 2B' + B'')$
- C $2M(1) + M(3) = Mg + 2Fe^{2+} \text{ } \square (\equiv 2C' + C'')$
- D $2M(1) + M(3) = 3Fe^{2+}$

In principle, both B and C should be resolvable into two components (B' , B'' ; C' , C'') that depend on whether or not the unique atom is at an M(1) or M(3) site. No such fitting procedure has been used. The total iron content of

the M(1) and M(3) positions in a binary (Mg,Fe) amphibole solid solution is given by

$$T = B + 2C + 3D \quad (15)$$

If the total Fe content of the amphibole is known from the chemical analysis, the Fe content of the M(2) + M(4) sites may be derived by difference.

Consider the equations relating peak intensity to mole fraction:

$$\begin{aligned} A &= \mu_1^2 \mu_3 = (1 - \phi_1)^2 (1 - \phi_3) \\ B &= \mu_1^2 \phi_3 + 2\mu_1 \phi_1 \mu_3 \\ &= (1 - \phi_1)^2 \phi_3 + 2(1 - \phi_1) \phi_1 (1 - \phi_3) \end{aligned} \quad (16)$$

$$\begin{aligned} C &= \phi_1^2 \mu_3 + 2\mu_1 \phi_1 \phi_3 = \phi_1^2 (1 - \phi_3) + 2(1 - \phi_1) \phi_1 \phi_3 \\ D &= \phi_1^2 \phi_3 = \phi_1^2 \phi_3 \end{aligned}$$

where μ_i and ϕ_i are the Mg and Fe^{2+} occupancies of the M(i) site. As $\phi_1 = 1/2(T - \phi_3)$, where T is known from the bulk composition, each of the peak intensities can be related to the single variable ϕ_3 . Thus four values of ϕ_3 are obtained, fairly precise estimates of the site-occupancies. An alternate method of obtaining site-occupancies using the intensity ratios of peaks B and C was developed by Strens (1966, 1974), but this has been disputed by Law (1976).

Clustering is the tendency for arrangements of like cations (*e.g.*, FeFeFe, MgMgMg) to occur more often than expected for random mixing. Strens (1966) noted that the infrared technique was sensitive to this effect, and suggested that clustering of Fe^{2+} or Mg in amphiboles is indicated if observed intensities of the D or A bands (D_o and A_o) exceed the values (D_c or A_c) calculated assuming random mixing. At this stage, it seemed that the presence or absence of clustering was an additional piece of information that could be derived from the band intensities. However, Law (1976) questioned the validity of this criterion for clustering, and Whittaker (1979) showed that the presence of clustering affects the relative intensity of all bands in the OH spectrum. This means that the procedure of Law (1976) that was outlined above for the derivation of M(1) and M(3) site-occupancies in amphiboles is only valid in the absence of cation clustering (or anticlustering: the mutual avoidance of like cations). To summarize the results of Whittaker (1979), clustering of Fe increases the intensity of *both* the A and D bands (although not equally), and also affects the intensities of the B and C bands in a complex manner that is a function of the bulk composition of the mineral. These results were for one particular model of cation interaction; as indicated by Whittaker (1979), other models are possible, leading to different but equally complex band intensity behavior. Considering the large number of factors that can affect the band intensities, it is questionable whether or not the spectrum contains sufficient information to derive a unique model. Certainly more work is required in

this vein if the OH band infrared method is going to produce quantitative site-occupancies for minerals in which clustering has not been disproved by other means (e.g., STEM with analytical capability).

The precision of the OH infrared method is not well-documented. The two examples given by Law (1976) have standard deviations of 0.02 and ~ 0.06 atoms/site respectively (ignoring the uncertainty in the bulk composition of the minerals). The precision of site-occupancy determinations will be a function of the bulk composition of and ordering pattern exhibited by the mineral, and a general statement of precision is not possible.

Although the arguments outlined above were developed for amphiboles, they are applicable in principle to other similar structure types. If clustering proves to be a common effect, it will almost certainly preclude any widespread use of the OH band infrared method for quantitative characterization of cation ordering without considerable development in the method of spectrum analysis. On the other hand, if the absence of clustering can be demonstrated (or assumed for qualitative work), this is an extremely useful technique, particularly for fine-grained material with ordering of non-Mössbauer sensitive species.

Electronic absorption spectroscopy

The 3d-orbitals of a transition metal ion are energetically degenerate in a spherically symmetric electric potential field. Application of an electric potential field of lower symmetry removes this degeneracy and leads to a splitting of the orbital energy levels. When light passes through a crystal containing a transition metal ion, certain wave lengths are absorbed by transition of electrons between the ground and excited states of the ion. As the character and amount of separation of the orbital energy levels is a function of the potential field applied by the crystal, occupancy of different sites in a crystal will produce absorption of different wavelengths of light. Hence optical absorption spectroscopy is of potential use to characterize site-occupancy in crystals both qualitatively (by observation and assignment of spectral bands to specific cations in specific sites—Burns, 1970a) and quantitatively (by comparison of spectral band intensities—Burns, 1970b). However, this method is not straightforward because the interpretation of the spectra is not simple, as indicated for example by the many conflicting studies on the orthopyroxenes (White and Keester, 1966, 1967; Bancroft and Burns, 1967; Burns, 1968, 1970a; Runciman *et al.*, 1973; Goldman and Rossman, 1976, 1977b).

Excitation occurs through interaction of the electric field of the incident radiation with a component of the dipole moment of the absorbing species; consequently the absorption is dependent both on orientation and the symmetry properties of the mineral. Thus for complete characterization of absorption, polarized absorption spectra are required. This is of particular importance in

minerals with polyvalent transition metal cations, in which the spectra may also be complicated by inter-element electron transitions, that is, charge transfer bands where the electron transitions take place from cation to anion, anion to cation or cation to cation. These transitions are particularly common when adjacent cations have variable valence states (e.g., Fe^{2+} and Fe^{3+} , Ti^{3+} and Ti^{4+}) and are a major cause of color and pleochroism in silicates (Manning and Nickel, 1969; Faye and Nickel, 1970; Burns, 1981). The intensity of this type of band is one to two orders of magnitude larger than the intensity of spin-allowed d-d bands. Thus overlap of these two types of band in an absorption spectrum can obscure the d-d transition bands. The occurrence of more than one type of transition-metal cation in the structure, as is common in many minerals, will further complicate the interpretation of the absorption spectra (*cf.* Moore and White, 1972). For the derivation of quantitative site-populations by this method, additional problems arise. The intensity of an absorption is a function of the probability of the transition. The transition probability is governed by the Laporte selection rule (King, 1964) which forbids transitions between 3d orbitals. When a transition-metal cation occupies a site without a center of symmetry, mixing the 3d and 4p orbitals allows a transition, the intensity of which is a function of the degree of 3d-4p mixing that is, in turn related to the deviation of the cation environment from centrosymmetry. Thus when a transition-metal cation occurs in more than one site in a crystal, the intensities of the d-d bands are a function of both the cation occupancies *and* the deviation of the cation environment from centrosymmetry. In centrosymmetric sites, some 3d-4p orbital mixing may occur by vibronic coupling and hence very weak bands can result from cations in these sites. Local disorder can also give rise to intensification of d-d bands in solid solutions; Robbins and Strens (1972) have noted this affect in micas and termed it "substitutional intensification". This could lead to non-linear relationship in Beer's law type plots (band intensity vs. concentration). Rossman (1975, 1976) has demonstrated tremendous enhancement of spin-forbidden d-d bands by antiferromagnetic exchange in hydroxy- and oxy-bridged Fe^{3+} clusters as compared with isolated Fe^{3+} polyhedra. These considerations suggest that if optical absorption spectroscopy is to be used for quantitative derivation of site-populations, it will be necessary to empirically calibrate the method using samples of known site-occupancy.

Extensive electronic absorption studies began in the mid-1960's (Farrel and Newnham, 1965; Burns, 1965; White and Keester, 1966) when there was a tendency to interpret the spectra purely in terms of d-d bands. Recognition of the importance of charge-transfer processes in minerals (Littler and Williams, 1965; Faye *et al.* 1968; Robbins and Strens, 1968) led to improvements in spectrum interpretation. Manning and Nickel (1969) and Faye and Nickel (1970) resolved the wide absorption

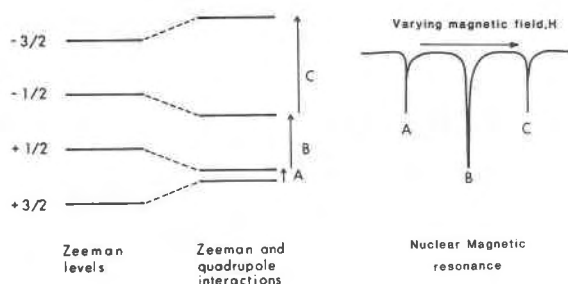


Fig. 4. Nuclear energy levels for a nucleus with spin $3/2$, showing the effect of the Zeeman and quadrupole interactions (left) and the resultant nuclear magnetic resonance (right).

bands in the spectra of pyroxenes and amphiboles into component peaks of narrower half-width, using a skewed Gaussian peak shape and a Dupont curve resolver. In a similar study on the olivines, Burns (1970b) used the resultant band intensities to assign Fe^{2+} site-occupancies to the M(1) and M(2) sites, evaluating the relationship between the peak area ratios and the Fe^{2+} site-occupancy ratios in two fayalites and assuming it to be constant across the series.

Goldman and Rossman (1977a,b, 1978) and Goldman *et al.* (1978) have shown that electronic absorption spectroscopy can be a powerful method for qualitatively assigning Fe^{2+} site-populations, and is particularly useful in assigning quadrupole split doublets in Mössbauer spectra to Fe^{2+} at specific sites in the structure under examination. Goldman and Rossman (1979) have also used this method to derive quantitative cation distributions in orthopyroxenes, correlating the intensity of bands due to Fe^{2+} at M(2) with the molar concentration of Fe^{2+} at this site. Their method was calibrated using orthopyroxenes of known site-occupancy.

This method has not had extensive use in quantitative site-population studies as yet but, as indicated by Rossman (1979), has considerable potential in this area. When the method requires unfolding of overlapping peaks as in the case of the olivines (Burns, 1970b), the computational problems are similar to those of the infrared method for hydroxyl-bearing silicates. When overlap problems can be avoided (Goldman and Rossman, 1979), the principal difficulty would appear to be adequately describing the shape of the background under the absorption band of interest, particularly when affected by the tail of a closely adjacent peak. In more complex solid solutions, substitutional broadening and "intensity borrowing" (Manning, 1973) may introduce considerable complexity into the calibration of this method.

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) is the resonance absorption and emission of electromagnetic radiation by an atomic nucleus in a magnetic field. An atomic nucleus has angular momentum that can be expressed as Ih ,

where I is called the nuclear spin quantum number and can take integer or half-integer values, and h is Planck's constant. As the nucleus is charged and has spin, it has a magnetic multipole moment that can interact with an applied magnetic field to produce a series of preferred orientations of the nuclear magnetic moment. These correspond to the number of quantum states indicated by I , the nuclear spin quantum number. Resonant absorption of energy corresponding to the energy separations of the quantum states can cause excitation between these states. Measurement of the energy absorbed by these transitions allows the characterization of the energy level separations. This is done by placing the specimen in an oscillating magnetic field and measuring the absorption of radio-frequency energy transmitted through the sample; thus the radio-frequency field is held constant and the magnetic field is varied.

There are two principal types of interaction between the nucleus and a magnetic field:

(1) interaction between the field and the nuclear magnetic dipole moment (Zeeman interaction) that results in $2I + 1$ equally spaced energy levels and one resonance absorption line.

(2) interaction between the field and the nuclear electric quadrupole moment. In general, this is a much smaller effect and can be treated as a second order perturbation on the Zeeman energy levels (Volkoff, 1953).

The effects of each interaction on the energy levels of a nucleus with spin $3/2$ is shown in Figure 4. The splitting of the energy levels is a function of the strength of the magnetic field and, in the case of the quadrupole interaction, the orientation of the magnetic field with regard to the environment of the nucleus. The energy separations between the perturbed Zeeman sublevels are no longer equal, and the single resonance line from the Zeeman interaction is split into $2I$ components. For half-integral spins, there is a central component and $2I - 1$ satellites symmetrically located about the central component; for integral spins, there are $2I$ shifted components.

Nuclear quadrupole resonance has been used qualitatively to measure order/disorder of atoms with nuclear spin $I > 1/2$. The central component ($-1/2 \leftrightarrow +1/2$ transition) depends only on second order terms of the perturbing electric quadrupole interaction, whereas the satellite lines ($\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ etc. transitions) depend on first order perturbation terms. Atomic disorder at surrounding sites results in different electric field gradients at crystallographically-equivalent positions throughout the crystal. This leads to broadening of the satellite lines, which may not be observed in crystals with considerable disorder. This effect has been used qualitatively to measure Al/Si order/disorder in feldspars (see Smith, 1974), and references therein), Al/Si disorder and Na positional disorder in nepheline (Brinkman *et al.*, 1972), Al/Si order in cordierite (Tsang and Ghose, 1972) and considerable disorder in tourmaline (Tsang and Ghose, 1973). Spin-echo spectra (using a

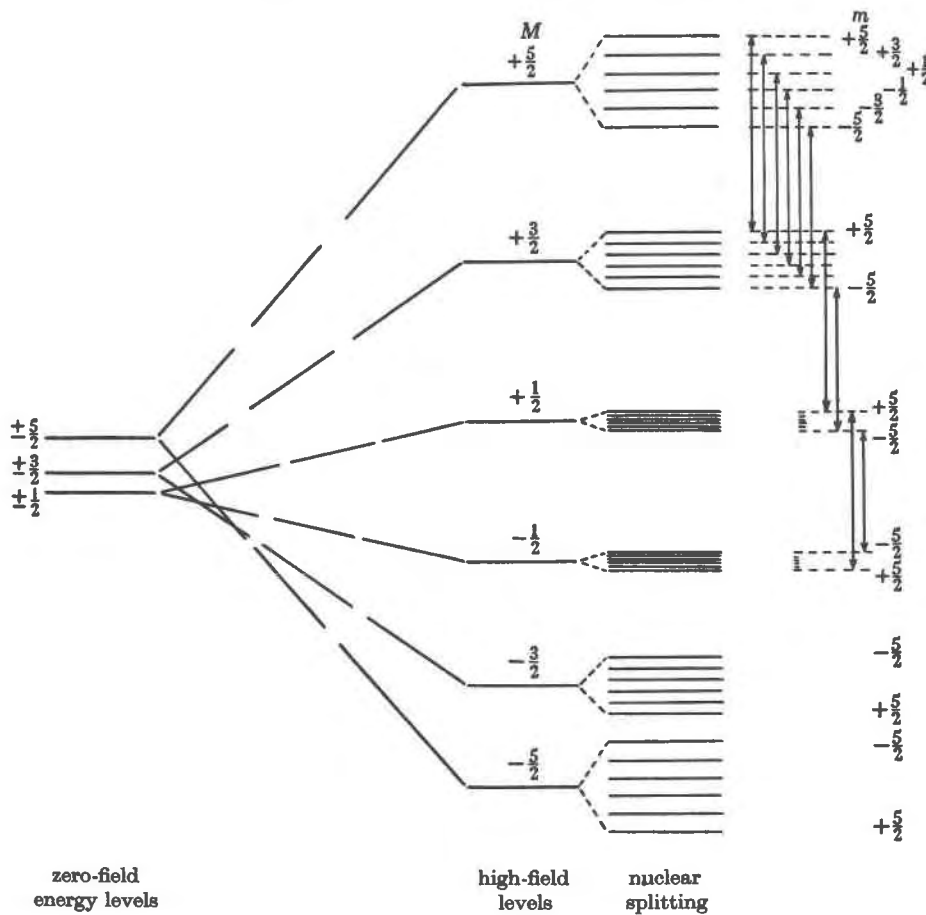


Fig. 5. Schematic energy-level diagram for Mn^{2+} showing the electronic levels in zero and in strong magnetic field together with the splitting due to nuclear spin; some typical transitions are shown by arrows (from Bleany and Ingram, 1951).

pulsed rather than a continuous radiofrequency field) have been used to characterize order/disorder in spinels (Rotter *et al.*, 1977; Shirakashi and Kubo, 1979).

Nuclear magnetic resonance can also be used to characterize order/disorder between diamagnetic and paramagnetic cations in crystals. The presence of paramagnetic ions in the immediate vicinity of the nucleus of interest considerably modifies the local magnetic field when compared with the field from an environment of diamagnetic ions. This change in the magnetic field in turn produces a change in the energy level separation(s) which causes a 'paramagnetic shift' in the resonance lines observed in the NMR spectrum. In a crystal with substitutional disorder at next-nearest-neighbor positions, the NMR spectrum consists of the diamagnetic spectrum plus one or more paramagnetically shifted spectra corresponding to the number of configurations of the next-nearest neighbors. The relative intensities of the various spectral lines are related to the frequency of occurrence of the next-nearest-neighbor configurations. Such paramagnetically shifted lines were recognized in

the ^{27}Al spectra of almandine (Ghose, 1964; Brinkman and Kaeser, 1972), and the relative intensities of the possible configurations correlated well with the chemical composition of the garnet. Sanz and Stone (1977) and Kalinichenko *et al.* (1977) used this technique with H^+ NMR spectra in micas and amphiboles to characterize Mg/Fe order/disorder at the octahedrally coordinated sites in these minerals. The problems associated with derivation of site-populations should be much the same as those encountered in the infrared method. Sanz and Stone (1977, 1979) have also shown the value of NMR spectroscopy applied to short-range order in minerals.

Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR) is the resonance absorption and emission of electromagnetic radiation by electrons of a paramagnetic ion. A paramagnetic ion with n unpaired electrons acts as a system with a spin $S = n/2$. The crystal field lifts the degeneracy of the electronic states and an applied magnetic field lifts the degeneracy of the spin states. Consequently the system

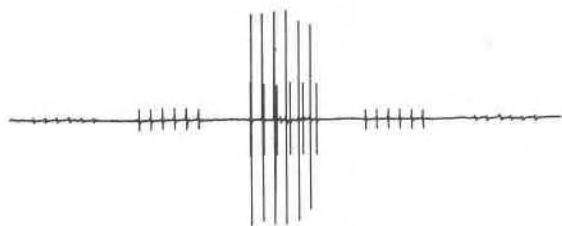


Fig. 6. Mn^{2+} electron paramagnetic resonance spectrum of diopside; note the two overlapping groups of hyperfine lines in the central region of the spectrum, due to Mn^{2+} at the M2 (strong) and M1 (weak) sites (from Ghose and Schindler, 1969).

has $S + 1$ energetically distinct levels; transitions between these levels are known as fine-structure lines. The presence of nuclear moments in the paramagnetic ion (or in the surrounding ligands) can also contribute to the local magnetic field at the electron. The number of possible orientations of a nuclear moment are $2I + 1$, and thus each fine-structure absorption line will be split into $2I + 1$ hyperfine lines. The selection rules allow transitions between levels of the same nuclear spin quantum number and differing by one in their electronic spin quantum number. A schematic energy level diagram for Mn^{2+} and the spectrum of Mn^{2+} in diopside (Ghose and Schindler, 1969) are shown in Figures 5 and 6. Fine-structure lines vary in intensity, whereas the hyperfine lines from a single fine-structure absorption are of equal intensity. General discussions of EPR and its application to mineralogy are given by Schindler (1968) and Ghose (1968). Most applications to mineralogy have involved Mn^{2+} or Fe^{3+} , although Ti^{3+} (Weeks, 1973), Eu^{2+} and Gd^{3+} (Morris, 1975) have been examined. This technique differs from the others outlined in this paper in that it is used to examine trace paramagnetic components in a diamagnetic structure. If the paramagnetic ions are not magnetically dilute, their magnetic moments interact and a broad structureless resonance results. The EPR is complementary to the other major component techniques described here.

Electron paramagnetic resonance has been used to semi-quantitatively measure order/disorder of atoms by comparing the intensities of absorption of atoms at different sites in a mineral. This is illustrated by the Mn^{2+} absorption in diopside shown in Figure 6. Superimposed on the strong central hyperfine sextet is a weaker hyperfine sextet with a slightly different spacing. Ghose and Schindler (1969) interpreted these as due to Mn^{2+} at the M2 and M1 sites respectively in diopside; from the relative intensity of the lines, site-occupancies were derived, assuming an equal transition probability at each site. There has not been sufficient work in this area to realistically evaluate the possible limits of accuracy and precision. However, this may change as there is considerable potential for application of EPR to magnetically dilute minerals, particularly gemstones.

Accuracy

An experimental result consists of the true value together with random and systematic errors characteristic of the experimental method. Precision is an estimate of the random error component. The systematic errors are far more difficult to examine. This can be done by analysis of standard samples in which the measured quantity is already known (*i.e.*, from the preparation method). This is feasible for diffraction methods by cation site-occupancy refinement in proven stoichiometric compounds in which cation disorder is not feasible (*e.g.*, disorder of Ca and S in $CaSO_4$), and for spectroscopic methods by examining ordered end-member compositions where all the relevant sites are completely occupied by the spectroscopically active species (*e.g.*, orthoferrosilite). There have been no systematic studies of this sort. The alternative method is to examine the same sample with a variety of techniques of approximately equal precision. The difference in the results is then a measure of the differences in their systematic errors, and the satisfactory agreement of several results suggests that systematic errors in each of the methods are not significant at the attained level of precision.

Table 1 shows selected results for X-ray diffraction and Mössbauer spectroscopy on the same samples, where the Mössbauer spectra were well-resolved and each determination is of comparable precision. The X-ray results for cummingtonite and anthophyllite have been modified slightly to account for small amounts of Ca and Mn; details of this procedure are given by Hawthorne (1983). The results are identical within the quoted precision, suggesting systematic errors well below the assigned precision, and hence accurate results. For more complex minerals, there are no suitable data for a comparison of this sort. Some available data are given in Table 2, but standard deviations are often not assigned, a Mn component is present in some of the X-ray site-occupancy determinations, and in the case of glaucophane the crystal

Table 1. Comparison of site-occupancy determinations of high precision in minerals with well-resolved Mössbauer spectra

Mineral	Site	X-ray	Mössbauer	Reference
Orthopyroxene	M1	0.743(3)	0.745(4)	(1)
	M2	0.957(3)	0.955(4)	
Cummingtonite	M(4)	0.76(-)	0.78(1)	(2,3)
	M(1,2,3)	0.21(-)	0.220(4)	
Grunerite	M(4)	0.985(8)	0.965(8)	(4,5)
	M(1,2,3)	0.826(10)	0.839(8)	
Anthophyllite	M4	0.511(6)	0.529(-)	(6,7)
	M1,2,3	0.028(3)	0.022(-)	

References: (1) Burnham *et al.* (1971); (2) Ghose (1961) and Fischer (1968), modified by author; (3) Ghose and Weidner (1972); (4) Finger (1969a); (5) Hafner and Ghose (1971); (6) Finger (1970), as modified by author; (7) Seifert (1978).

Table 2. Comparison of site-occupancy determinations in complex minerals

Mineral		X-ray	Mössbauer	Infrared
Manganooan ferro-actinolite	M(1)	0.61(-)Fe*	0.76(-)Fe ²⁺	0.66(6)Fe ²⁺
	M(2)	0.46(-)Fe*+0.16Fe ³⁺	0.29(-)Fe ²⁺	0.47(6)Fe ²⁺
	M(3)	0.58(-)Fe*	0.40(-)Fe ²⁺	0.23(6)Fe ²⁺
	Ref.	(1)	(2)	(3)
Holmquistite	M1	0.39(-)Fe* ₃₊	0.36(5)Fe ²⁺	-
	M2	0.065(-)Fe ³⁺	0.06(2)Fe ²⁺	-
	M3	0.56(-)Fe*	0.59(9)Fe ²⁺	-
	Ref.	(4)	(5)	-
Glaucophanes	M(1)	0.16(2)Fe ²⁺	0.19(-)Fe ²⁺	-
	M(2)	0.09(2)Fe ³⁺	0.15(-)Fe ³⁺	-
	M(3)	0.29(2)Fe ²⁺	0.32(-)Fe ²⁺	-
	Ref.	(6)	(7)	-

Fe* = Fe²⁺ = Mn. References: (1) Mitchell *et al.* (1971); (2) Burns and Greaves (1971); (3) Law (1976); (4) Irusteta and Whittaker (1975); (5) Law Whittaker (1981); (6) Papike and Clark (1988); (7) Bancroft and Burns (1969).

used in the X-ray study apparently deviated from the average chemistry of the bulk sample and so the results are not strictly comparable. The results for holmquistite agree fairly well. There is considerable variation among the different results for the manganooan ferro-actinolite, but without standard deviations it is not apparent whether or not these differences are significant; one might expect the standard deviations in the Mössbauer study to be at least as large as those of the holmquistite study, so possibly the differences are not significant. Certainly a comparative study of this sort on some of the more complex minerals by current techniques is desirable.

In well-characterized mineral groups, the accuracy of site-occupancy determination by structure refinement can be checked from mean bond-length constituent cation/anion radius relationships, where it is known that such relationships are well-behaved (*i.e.*, not significantly perturbed by substitutions at other sites in the structure). The sensitivity of this method depends on the difference in ionic radius of the cations/anions involved, and on the coordination number of the site. In some cases, ionic radii differences are sufficient to assess the accuracy of the method at the level of assigned precision (*e.g.*, Al/Si refinement using neutron diffraction data), but this is not generally the case. For such cases as Mg/Fe²⁺ or Al/Fe³⁺ ordering, where precisions of ~0.005 atoms per site can be expected from X-ray diffraction data, assessment of accuracy is an order of magnitude larger than the precision except perhaps in optimum cases where the structures are very well characterized.

Conclusions

The methods for site-population determination all have their specific advantages and disadvantages; there is no philosopher's stone for site-occupancy characterization. When introducing new techniques to this field, there has been a tendency in the past to overemphasize their utility

and gloss over some of the inherent difficulties. Experience should tell us that "methods of considerable potential" are also methods with considerable unrecognized problems.

Of the techniques surveyed here, single-crystal X-ray diffraction is the most widely applicable. Any binary combination of atoms differing significantly in atomic number can be handled, with site-occupancies determined fairly precisely (~0.005 for Mg/Fe site-occupancies, ~0.01 for Na/Ca site-occupancies). In addition, stereochemical information is derived and this can lead to further definition of site-occupancies and/or an internal check on the accuracy of the result. Single-crystal neutron diffraction is less widely used, but has similar characteristics and is particularly useful for site-occupancies involving Al/Si (precision ~0.03), Fe/Mn and Fe/Ti ordering. Mössbauer spectroscopy is highly specific in application, and most work has focussed on ordering of Fe²⁺ and Fe³⁺. However, the ubiquity of Mg/Fe²⁺ and Al/Fe³⁺ diadochy in minerals makes this an important technique in site-occupancy determination. The ability to accurately distinguish between Fe²⁺ and Fe³⁺ is of particular utility. In well-resolved spectra, Fe²⁺ site-occupancies can be determined with a precision of ~0.005. With decreasing spectral resolution, parameter correlation becomes a problem and the precision of site-occupancy determination decreases strongly. Hydroxyl-band infrared spectroscopy seems to be capable of adequate precision (~0.02 on Mg/Fe²⁺ site-occupancies). However, the method is perturbed by clustering and further development of this method to allow for this effect is necessary. Electronic absorption spectroscopy is now being used for quantitative site-occupancy determination, and there is potential here for further development. X-ray and neutron diffraction powder profile-refinement, γ -ray diffraction, X-ray photoelectron diffraction, nuclear magnetic resonance spectroscopy and electron paramagnetic resonance spectroscopy have potential for quantitative characterization of site-occupancies, but more development is required.

The determination of site-occupancies in minerals is not a trivial problem, particularly in the more chemically complex species. Any single method can only resolve binary site-occupancies sensitive to that particular technique. Complete experimental characterization of site-occupancies frequently requires a combination of several techniques that should be regarded as complementary rather than competitive. The very specific sensitivity of many of the spectroscopic techniques make them a natural counterpart to both diffraction techniques and other spectroscopic methods. The difficulties and ambiguities involved in an experimental method can often be substantially reduced by using a combination of experimental techniques pertinent to the specific problem at hand. The utility of this approach is evident from several studies (Bancroft *et al.*, 1967a; Bancroft and Burns, 1969; Hawthorne and Grundy, 1977; Goldman and Rossman,

1977a; Goldman *et al.*, 1977), the combination of methods leading to a much better characterization of site-populations than would otherwise have occurred.

Acknowledgments

The author is particularly grateful to Dr. Wayne Dollase whose comments greatly improved an earlier version of this paper. I would like to thank George R. Rossman and Associate Editor Subrata Ghose for their comments. Financial support during this work was provided by a Research Fellowship and grant to the author from the Natural Sciences and Engineering Research Council of Canada.

References

- Adams, J. M., Evans, S., and Thomas, J. M., (1978). X-ray photoelectron diffraction: a new technique for structural studies of complex solids. *Journal of the American Chemical Society*, 100, 3260–3265.
- Baker, R. J., and Stevens, J. G., (1977). ^{121}Sb Mössbauer spectroscopy. Part II. Comparison of structure and bonding in Sb(III) and Sb(V) minerals. *Revue de Chimie Minerale*, 14, 339–346.
- Bancroft, G. M., (1967). Quantitative estimates of site-populations in an amphibole by the Mössbauer effect. *Physical Review*, 26A, 17–18.
- Bancroft, G. M., (1970). Quantitative site-populations in silicate minerals by the Mössbauer effect. *Chemical Geology*, 5, 255–258.
- Bancroft, G. M., (1973). *Mössbauer Spectroscopy. An Introduction for Inorganic Chemists and Geologists.* McGraw-Hill Book Co. Inc., New York.
- Bancroft, G. M., Brown, J. R., and Fyfe, W. S., (1979). Advances in, and applications of, X-ray photoelectron spectroscopy (ESCA) in mineralogy and geochemistry. *Chemical Geology*, 25, 527–543.
- Bancroft, G. M., and Burns, R. G., (1967). Interpretation of the electronic spectra of iron in pyroxenes. *American Mineralogist*, 52, 1578–1587.
- Bancroft, G. M., and Burns, R. G., (1969). Mössbauer and absorption spectral study of alkali amphiboles. *Mineralogical Society of America Special Paper*, 2, 137–148.
- Bancroft, G. M., Burns, R. G., Maddock, A. G., and Strens, R. G. J., (1966). Cation distribution in anthophyllite from Mössbauer and infrared spectroscopy. *Nature*, 212, 913–915.
- Bancroft, G. M., Burns, R. G., and Maddock, A. G., (1967a). Determination of the cation distribution in the cummingtonite-grunerite series by Mössbauer spectroscopy. *American Mineralogist*, 52, 1009–1026.
- Bancroft, G. M., Maddock, A. G., and Burns, R. G., (1967b). Applications of the Mössbauer effect to silicate mineralogy—I. Iron silicates of known crystal structure. *Geochimica et Cosmochimica Acta*, 31, 2219–2246.
- Bassett, W. A., (1960). Role of hydroxyl orientation in mica alteration. *Bulletin of the Geological Society of America*, 71, 449–456.
- Baur, W. H., (1974). The geometry of polyhedral distortions. Predictive relationships for the phosphate group. *Acta Crystallographica*, B30, 1195–1215.
- Baur, W. H., (1978). Variation in mean Si–O bond lengths in silicon-oxygen tetrahedra. *Acta Crystallographica*, B34, 1751–1756.
- Blaha, J. J., and Rosasco, G. J., (1978). Raman microprobe spectra of individual microcrystals and fibers of talc, tremolite, and related silicate minerals. *Analytical Chemistry*, 50, 892–896.
- Blume, M., (1966). Magnetic relaxation and asymmetric quadrupole doublets in the Mössbauer effect. *Physics Letters*, 14, 96–98.
- Brinkmann, D., and Kaeser, L., (1972). Hyperfine interactions of Al and Si in the paramagnetic garnet almandine ($\text{Fe, Mg}_3\text{Al}_2(\text{SiO}_4)_3$). *Solid State Communications*, 11, 1519–1521.
- Brinkmann, D., Ghose, S., and Laves, F., (1972). Nuclear magnetic resonance of ^{23}Na , ^{27}Al , and ^{29}Si and cation disorder in nepheline. *Zeitschrift für Kristallographie*, 135, 208–218.
- Brown, G. E., (1978). Olivines and silicate spinels. *Reviews in Mineralogy*, 5, 275–381.
- Brown, G. E., Hamilton, W. C., Prewitt, C. T., and Sueno, S., (1974). Neutron diffraction study of Al/Si ordering in sanidine: a comparison with X-ray diffraction data. In W. S. Mackenzie and J. Zussman, Eds., *The Feldspars: Proceedings of the NATO Advanced Study Institute*, p. 68–80. Manchester University Press.
- Brown, I. D., and Shannon, R. D., (1973). Empirical bond length-bond strength curves for oxides. *Acta Crystallographica*, B29, 566–585.
- Burnham, C. W., (1962). Temperature parameters of silicate crystal structures (abstr.). *American Mineralogist*, 47, 282.
- Burnham, C. W., and Radoslovich, E. W., (1963). Crystal structures of coexisting muscovite and paragonite. *Carnegie Institute of Washington Year Book*, 62, 232–236.
- Burnham, C. W., Ohashi, Y., Hafner, S. S., and Virgo, D., (1971). Cation distribution and atomic thermal vibrations in an iron-rich orthopyroxene. *American Mineralogist*, 56, 850–876.
- Burns, R. G., (1965). *Electronic Spectra of Silicate Minerals: Applications of Crystal Field Theory to Aspects of Geochemistry.* Ph.D. Thesis, University of California, Berkeley, California.
- Burns, R. G., (1968). Enrichment of transition-metal ions in silicate crystal structures. In L. H. Ahrens, Ed., *Origin and Distribution of the Elements*, p. 1151–1164. Pergamon Press, Oxford.
- Burns, R. G., (1970a). *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press, Cambridge.
- Burns, R. G., (1970b). Crystal field spectra and evidence of cation ordering in olivine minerals. *American Mineralogist*, 55, 1608–1632.
- Burns, R. G., (1981). Intervalence transitions in mixed-valence minerals of iron and titanium. *Annual Reviews of Earth and Planetary Sciences*, 9, 345–383.
- Burns, R. G., and Greaves, C. J., (1971). Correlations of infrared and Mössbauer site-population measurements of actinolites. *American Mineralogist*, 56, 2010–2033.
- Burns, R. G., and Huggins, F. A., (1972). Cation determinative curves for Mg-Fe-Mn olivines from vibrational spectra. *American Mineralogist*, 57, 967–985.
- Burns, R. G., and Prentice, F. J., (1968). Distribution of iron cations in the crocidolite structure. *American Mineralogist*, 53, 770–776.
- Burns, R. G., and Strens, R. G. J., (1966). Infrared study of the hydroxyl bands in clinoamphiboles. *Science*, 153, 890–892.
- Cameron, M., and Papike, J. J., (1981). Structural and chemical variations in pyroxenes. *American Mineralogist*, 66, 1–50.
- DeAngelis, B. A., Keramidis, V. G., and White, W. B., (1971). Vibrational spectra of spinels with 1:1 ordering on tetrahedral

- sites. *Journal of Solid State Chemistry*, 3, 358–363.
- DeCoster, M., Pollak, H., and Amelinckx, S., (1963). A study of Mössbauer absorption in iron silicates. *Physica Status Solidi*, 3, 283–288.
- Dollase, W. A., (1973). Mössbauer spectra and iron distribution in the epidote-group minerals. *Zeitschrift Für Kristallographie*, 138, 41–63.
- Dollase, W. A., (1975). Statistical limitations of Mössbauer spectral fitting. *American Mineralogist*, 60, 257–264.
- Duncan, J. F., Freeman, A. G., and Johnston, J. H., (1973). Specific radiation crystallography (SRC). *Chemistry in New Zealand*, 1973, 45–49.
- Duncan, J. F., Freeman, A. G., and Johnston, J. H., (1975). Identification of atomic environments by anomalous X-ray scattering and Mössbauer diffraction methods. In S. Ramaseshan and S. C. Abrahams, Eds., *Anomalous Scattering*, p. 163–174. Munksgaard, Copenhagen.
- Duncan, J. F., and Johnston, J. H., (1973). The determination of the cation distribution in olivine from single crystal Mössbauer studies. *Australian Journal of Chemistry*, 26, 231–239.
- Duncan, J. F., and Johnston, J. H., (1974). Single-crystal ^{57}Fe Mössbauer studies of the site positions in cordierite. *Australian Journal of Chemistry*, 27, 249–258.
- Estep, P. A., Kovach, J. J., and Karr, Jr. C., (1971). Infrared vibrational spectroscopic studies of minerals from Apollo 11 and Apollo 12 lunar samples. *Proceedings of the Second Lunar Science Conference*, 3, 2137–2151.
- Evans, B. J., Ghose, S., and Hafner, S. S. (1967). Hyperfine splitting of ^{57}Fe and Mg-Fe order-disorder in orthopyroxenes. *Journal of Geology*, 75, 306–322.
- Farmer, V. C., and Velde, B., (1973). Effects of structural order and disorder on the infrared spectra of brittle micas. *Mineralogical Magazine*, 39, 282–288.
- Farrell, E. F., and Newnham, R. E., (1965). Crystal field spectra of chrysoberyl, alexandrite, peridot and sinhalite. *American Mineralogist*, 50, 1972–1981.
- Farrel, E. F., Fang, J. H., and Newnham, R. E., (1963). Refinement of the chrysoberyl structure. *American Mineralogist*, 48, 804–810.
- Faye, G. H., Manning, P. G., and Nickel, E. H., (1968). The polarized optical absorption spectra of tourmaline, cordierite, chloritoid and vivianite: ferrous-ferric interaction as a source of pleochroism. *American Mineralogist*, 53, 1174–1201.
- Finger, L. W., (1969a). The crystal structure and cation distribution of a grunerite. *Mineralogical Society of America Special Paper*, 2, 95–100.
- Finger, L. W., (1969b). Determination of cation distribution by least-squares refinement of single-crystal X-ray data. *Carnegie Institute of Washington Year Book*, 67, 216–217.
- Finger, L. W., (1969c). *RFINE*. A Fortran IV computer program for structure factor calculation and least-squares refinement of crystal structure. Geophysical Laboratory, Carnegie Institute of Washington (unpublished).
- Finger, L. W., (1970). Refinement of the crystal structure of an anthophyllite. *Carnegie Institute of Washington Year Book*, 68, 283–288.
- Finger, L. W., and Prince, E., (1975). A system of Fortran IV computer programs for crystal structure computations. NBS Technical Note 854.
- Fischer, K. F., (1963). Least-squares refinement of atomic scattering factors: possibilities, techniques, and applications (abstr.). *American Crystallographic Association Abstracts, Cambridge Meeting*, 41–42.
- Fischer, K. F., (1965). Röntgenographische Unterscheidung von Silizium und Aluminium-Punktlagen durch Verfeinerung des atomaren Streuvermögens. *Tschermaks Mineralogische und Petrographische Mitteilungen*, 10, 203–208.
- Fischer, K. F., (1966). A further refinement of the crystal structure of cummingtonite, $(\text{Mg,Fe})_7(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$. *American Mineralogist*, 51, 814–818.
- Fischer, K. F., (1968). Refinement of scattering factors of atoms and equipoints in crystal structures by least-squares techniques. *Zeitschrift für Kristallographie*, 127, 110–120.
- Fischer, K. F., and Zehme, H., (1967). Röntgenographische Untersuchung der Si-Al-Verteilung in einem Mikroklin durch Verfeinerung des atomaren Streuvermögens. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 47, 163–167.
- Ghose, S., (1961). The crystal structure of cummingtonite. *Acta Crystallographica*, 14, 622–627.
- Ghose, S., (1964). Nuclear magnetic resonance spectrum of ^{27}Al in a natural almandine garnet $(\text{Fe}^{\text{II}},\text{Mg})_3\text{Al}_2(\text{SiO}_4)_3$. *Solid State Communications*, 2, 361–362.
- Ghose, S., (1968). Application of electron paramagnetic resonance in silicate minerals. *Short Course Lecture Notes, Resonance Spectroscopy in Mineralogy, G1–G15*. American Geological Institute.
- Ghose, S., and Hafner, S. S., (1967). Mg^{2+} – Fe^{2+} distribution in metamorphic and volcanic pyroxenes. *Zeitschrift für Kristallographie*, 125, 157–162.
- Ghose, S., and Hellner, E., (1959). The crystal structure of grunerite and observations on the Mg–Fe distribution. *Journal of Geology*, 67, 691–701.
- Ghose, S., and Schindler, P., (1969). Determination of the distribution of trace amounts of Mn^{2+} in diopsides by electron paramagnetic resonance. *Mineralogical Society of America Special Paper*, 2, 51–58.
- Ghose, S., and Weidner, J. R., (1972). Mg^{2+} – Fe^{2+} order-disorder in cummingtonite, $(\text{Mg,Fe})_7(\text{Si}_8\text{O}_{22})(\text{OH})_2$: a new geothermometer. *Earth and Planetary Science Letters*, 16, 346–354.
- Gibb, T. C., and Greenwood, N. N., (1966). Chemical applications of the Mössbauer effect. Part 2—Oxidation states of iron in crocidolite and amosite. *Transactions of the Faraday Society*, 61, 1317–1323.
- Goldman, D. A., and Rossman, G. R., (1976). Identification of a mid-infrared electronic absorption band of Fe^{2+} in the distorted M(2) site of orthopyroxene, $(\text{Mg,Fe})\text{SiO}_3$. *Chemical Physics Letters*, 41, 474–475.
- Goldman, D. A. and Rossman, G. R., (1977a). The identification of Fe^{2+} in the M(4) site of calcic amphiboles. *American Mineralogist*, 62, 205–216.
- Goldman, D. A., and Rossman, G. R., (1977b). The spectra of iron in orthopyroxene revisited: the splitting of the ground state. *American Mineralogist*, 62, 151–157.
- Goldman, D. A., and Rossman, G. R., (1978). The site distribution of iron and anomalous biaxiality in osumilite. *American Mineralogist*, 63, 490–498.
- Goldman, D. R., and Rossman, G. R., (1979). Determination of quantitative cation distribution in orthopyroxenes from electronic absorption spectra. *Physics and Chemistry of Minerals*, 4, 43–53.
- Goldman, D. G., Rossman, G. R., and Dollase, W. A. (1977). Channel constituents in cordierite. *American Mineralogist*, 62, 1144–1157.
- Hafner, S. S., and Ghose, S., (1971). Iron and magnesium distribution in cummingtonites $(\text{Fe,Mg})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. *Zeitsch-*

- rift für Kristallographie, 133, 301–326.
- Hamilton, W. C., and Ibers, J. A., (1968). Hydrogen Bonding in Solids. Benjamin, New York.
- Hawthorne, F. C., (1981a). Some systematics of the garnet structure. *Journal of Solid State Chemistry*, 37, 157–164.
- Hawthorne, F. C., (1981b). Amphibole spectroscopy. *Reviews in Mineralogy*, 9A, 103–139.
- Hawthorne, F. C., (1983). The crystal chemistry of the amphiboles. *Canadian Mineralogist*, 23, (in press).
- Hawthorne, F. C., and Grundy, H. D., (1977). The crystal structure and site-chemistry of a zincian tirodite by least-squares refinement of X-ray and Mössbauer data. *Canadian Mineralogist*, 15, 309–320.
- Huggins, F. E., (1973). Cation order in olivines: evidence from vibrational spectra. *Chemical Geology*, 11, 99–109.
- Irusteta, M. C., and Whittaker, E. J. W., (1975). A three-dimensional refinement of the structure of holmquistite. *Acta Crystallographica*, B31, 145–150.
- Johnston, J. H., and Duncan, J. F., (1975). Manganese ion site distribution studies in tourmaline by anomalous X-ray scattering methods. *Journal of Applied Crystallography*, 8, 469–472.
- Kalinichenko, A. M., Banzarakshiev, N. Yu., Matyash, I. V., Litvin, A. L., and Pol'shin, E. V., (1977). Refinement of the structural characteristics of hornblende by reference to proton-magnetic-resonance data. *Soviet Physics Crystallography*, 22, 225–226.
- King, G. W., (1964). *Spectroscopy and Molecular Structure*. Holt, Rinehart and Winston Inc., New York.
- Kitamura, M., Tokonami, M., and Morimoto, N., (1975). Distribution of titanium atoms in oxy-kaersutite. *Contributions to Mineralogy and Petrology*, 51, 167–172.
- Kosoi, A. L., Malkova, L. A. and Frank-Kamenetskii, V. A., (1974). Crystal-chemical characteristics of rhombic pyroxenes. *Soviet Physics Crystallography*, 19, 171–174.
- Kovach, J. J., Hiser, A. L., and Karr, Jr., C., (1975). Far-infrared spectroscopy of minerals. In C. Karr, Jr., Ed., *Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals*, p. 231–254. Academic Press, New York.
- Law, A. D., (1973). Critical evaluation of "statistical best fits" to Mössbauer spectra. *American Mineralogist*, 58, 128–131.
- Law, A. D., (1976). A model for the investigation of hydroxyl spectra of amphiboles. In R. G. J. Strens, Ed., *The Physics and Chemistry of Minerals and Rocks*, p. 677–686. Wiley, London.
- Law, A. D. and Whittaker, E. J. W., (1981). Studies of the orthoamphiboles I.—The Mössbauer and infrared spectra of holmquistite. *Bulletin de la Société Française de Minéralogie et de Cristallographie*, 104, 381–386.
- Littler, J. G. F., and Williams, R. J. P., (1965). Electrical and optical properties of crocidolite and some other compounds. *Journal of the Chemical Society*, 1965, 6368–6371.
- Manning, P. G., (1973). Intensities and half-widths of octahedral $-Fe^{3+}$ crystal-field bands and Racah parameters as indicators of next-nearest-neighbour interactions in garnets. *Canadian Mineralogist*, 12, 215–218.
- Manning, P. G., and Nickel, E. H., (1969) A spectral study of the origin of colour and pleochroism of a titanite from Kaiserstuhl and of a riebeckite from St. Peter's Dome, Colorado. *Canadian Mineralogist*, 10, 71–83.
- Martin, R. F., (1970). Cell parameters and infrared absorption of synthetic high to low albites. *Contributions to Mineralogy and Petrology*, 26, 62–74.
- Mitchell, J. T., Bloss, F. D., and Gibbs, G. V., (1971). Examination of the actinolite structure and four other C2/M amphiboles in terms of double bonding. *Zeitschrift für Kristallographie*, 133, 273–300.
- Moore, R. K., and White, W. B., (1972). Electronic spectra of transition metal ions in silicate garnets. *Canadian Mineralogist*, 11, 791–811.
- Morris, R. V., (1975). Electron paramagnetic resonance study of the site preferences of Gd^{3+} and Eu^{2+} in polycrystalline silicate and aluminate minerals. *Geochimica et Cosmochimica Acta*, 39, 621–634.
- Nickel, E. H., (1970). The effect of charge-transfer processes on the colour and pleochroism of amphiboles. *Canadian Mineralogist*, 10, 616–635.
- Nord, A. G., (1977). The cation distributions in $Zn_2Mg(PO_4)_2$ determined by X-ray profile-fitting refinements. *Materials Research Bulletin*, 12, 563–568.
- Nord, A. G., and Stefanidis, T., (1980). The cation distribution in two $(Co,Mg)_3(PO_4)_2$ solid solutions. *Zeitschrift für Kristallographie*, 153, 141–149.
- Novak, G. A., and Gibbs, G. V., (1971). The crystal chemistry of the silicate garnets. *American Mineralogist*, 56, 791–823.
- Papike, J. J., and Clark, J. R., (1968). The crystal structure and cation distribution of glaucophane. *American Mineralogist*, 53, 1156–1173.
- Phillips, M. W., and Ribbe, P. H., (1973). The structures of monoclinic potassium-rich feldspars. *American Mineralogist*, 58, 263–270.
- Prince, E., Donnay, G., and Martin, R. F., (1973). Neutron diffraction refinement of an ordered orthoclase. *American Mineralogist*, 58, 500–507.
- Pollak, H., DeCoster, M., and Amelinckx, A., (1962). Mössbauer effect in biotite. *Physica Status Solidi*, 2, 1653–1659.
- Rietveld, H. M., (1969). A profile refinement method for nuclear and magnetic structures. *Journal of Applied Crystallography*, 2, 65–71.
- Robbins, D. W., and Strens, R. G. J., (1968). Polarization dependence and oscillator strengths of metal-metal charge transfer in iron (II, III) silicate minerals. *Chemical Communications*, 1968, 508–509.
- Robbins, D. W., and Strens, R. G. J., (1972). Charge-transfer in ferromagnesian silicates: the polarized electronic spectra of trioctahedral micas. *Mineralogical Magazine*, 38, 551–563.
- Rollet, J. S., (1970). Least-squares procedures in crystal structure analysis. In F. R. Ahmed, Ed., *Crystallographic Computing*, p. 167–191. Munksgaard, Copenhagen.
- Rosenburg, P. E., and Foit, F. F., (1977). $Fe^{2+} - F$ avoidance in silicates. *Geochimica et Cosmochimica Acta*, 41, 345–346.
- Rossmann, G. R., (1975). Spectroscopic and magnetic studies of ferric iron hydroxy sulfates: intensification of color in ferric iron clusters bridged by a single hydroxide ion. *American Mineralogist*, 60, 698–704.
- Rossmann, G. R. (1976). The optical spectroscopic comparison of the ferric iron tetrameric clusters in amarantite and leucophosphate. *American Mineralogist*, 61, 933–938.
- Rossmann, G. R., (1979). Structural information from quantitative infrared spectra of minerals. *Transactions of the American Crystallographic Association*, 15, 77–91.
- Rotter, M., Sedlak, B., and Simsa, Z., (1977). NMR of Mn^{3+} ions in B-sites of Mn-ferrites. *Czechoslovak Journal of Physics*, B27, 1180–1192.
- Rowbotham, G., and Farmer, V. C., (1973). The effect of "A" site occupancy on the hydroxyl stretching frequency in clino-amphiboles. *Contributions to Mineralogy and Petrology*, 38,

- 147-149.
- Rouxhet, P. G., (1970). Hydroxyl stretching bands in micas: a quantitative interpretation. *Clay Minerals*, 8, 375-387.
- Runciman, W. A., Sengupta, D., and Marshall, M., (1973). The polarized spectra of iron in silicates. I. Enstatite. *American Mineralogist*, 58, 444-450.
- Sanz, J. and Stone, W. E. E., (1977). NMR study of micas, I. Distribution of Fe^{2+} ions on the octahedral sites. *Journal of Chemical Physics*, 67, 3739-3745.
- Sanz, J., and Stone, W. E. E., (1979). NMR study of micas, II. Distribution of Fe^{2+} , F^- and OH^- in the octahedral sheet of phlogopites. *American Mineralogist*, 64, 119-126.
- Schindler, P., (1968). Electron paramagnetic resonance (electron spin resonance). Short Course Lecture Notes, Resonance Spectroscopy in Mineralogy, SI-S27. American Geological Institute.
- Seifert, F., (1978). Equilibrium Mg- Fe^{2+} cation distribution in anthophyllite. *American Journal of Science*, 278, 1323-1333.
- Semet, M. P., (1973). A crystal chemistry study of synthetic magnesiohastingsite. *American Mineralogist*, 58, 480-494.
- Shannon, R. D., (1975). Systematic studies of interatomic distances in solids. In R. G. J. Strens, Ed., *Physics and Chemistry of Minerals and Rocks*, p. 403-431. Princeton University Press, New Jersey.
- Shannon, R. D., (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751-757.
- Shirakashi, T., and Kubo, T., (1979). Cation distribution in franklinite by nuclear magnetic resonance. *American Mineralogist*, 64, 599-603.
- Smith, J. V., (1974). *Feldspar Minerals I. Crystal Structure and Physical Properties*. Springer-Verlag, New York.
- Steinfink, H., (1962). Crystal structure of a trioctahedral mica: Phlogopite. *American Mineralogist*, 47, 886-894.
- Stevens, J. G., and Macintosh, J. R., (1977). Mössbauer studies of silver-antimony-sulfide minerals. *Inorganic and Nuclear Chemistry Letters*, 13, 595-598.
- Strens, R. G. J., (1966). Infrared study of cation ordering and clustering in some (Fe,Mg) amphibole solid solutions. *Chemical Communications*, 15, 519-520.
- Strens, R. G. J., (1974). The common chain, ribbon, and ring silicates. In V. C. Farmer, Ed., *The Infrared Spectra of Minerals*, p. 305-330. Mineralogical Society Monography, 4, Mineralogical Society, London.
- Tsang, T., and Ghose, S., (1972). Nuclear magnetic resonance of ^1H and ^{27}Al and Al-Si order in low cordierite, $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18} \cdot n\text{H}_2\text{O}$. *Journal of Chemical Physics*, 56, 3329-3332.
- Tsang, T., and Ghose, S., (1973). Nuclear magnetic resonance of ^1H , ^7Li , ^{11}B , ^{23}Na and ^{27}Al in tourmaline (elbaite). *American Mineralogist*, 58, 224-229.
- Vedder, W., (1964). Correlations between infrared spectrum and chemical composition of mica. *American Mineralogist*, 49, 736-768.
- Virgo, D., and Hafner, S. S., (1968). Re-evaluation of the cation distribution in orthopyroxenes by the Mössbauer effect. *Earth and Planetary Science Letters*, 4, 265-269.
- Virgo, D., and Hafner, S. S., (1969). Fe^{2+} , Mg order-disorder in heated orthopyroxenes. *Mineralogical Society of America Special Paper* 2, 67-81.
- Volkoff, G. M., (1953). Second order nuclear quadrupole effects in single crystals. *Canadian Journal of Physics*, 31, 820-836.
- Waser, J., (1963). Least-squares refinement with subsidiary conditions. *Acta Crystallographica*, 16, 1091-1094.
- Weeks, R. A., (1973). Paramagnetic resonance spectra of Ti^{3+} , Fe^{3+} , and Mn^{2+} in lunar plagioclases. *Journal of Geophysical Research*, 78, 2393-2401.
- Wertheim, G. K., (1964). *The Mössbauer Effect, Principles and Applications*. Academic Press, New York.
- White, W. B., (1967). Application of infrared spectroscopy to order-disorder problems in simple ionic solids. *Materials Research Bulletin*, 2, 381-394.
- White, W. B., (1974). Order-disorder effects. In V. C. Farmer, Ed., *The Infrared Spectral of Minerals*, p. 87-110. Mineralogical Society Monograph, 4, Mineralogical Society, London.
- White, W. B., (1975). Structural interpretation of lunar and terrestrial minerals by raman spectroscopy. In C. Karr, Jr., Ed., *Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals*, p. 197-229. Academic Press, New York.
- White, W. B., and DeAngelis, B. A., (1967). Interpretation of the vibrational spectra of spinels. *Spectrochimica Acta*, 23A, 985-995.
- White, W. B., and Keester, K. L., (1966). Optical absorption spectra of iron in the rock-forming silicates. *American Mineralogist*, 51, 774-791.
- White, W. B., and Keester, K. L., (1967). Selection rules and site assignments for the spectra of ferrous iron in pyroxenes. *American Mineralogist*, 52, 1508-1514.
- White, W. B., and Keramidas, V. G., (1972). Application of infrared and Raman spectroscopy to the characterization of order-disorder in high temperature oxides. *Proceedings of the Fifth Materials Research Symposium, National Bureau of Standards Special Publication*, 364, 113-126.
- Whittaker, E. J. W., (1949). The structure of Bolivian crocidolite. *Acta Crystallographica*, 2, 312-317.
- Whittaker, E. J. W., (1975). Determination of atomic occupancies. In D. G. Fraser, Ed., *Thermodynamics in Geology*, p. 99-113, Reidel, Dordrecht, The Netherlands.
- Whittaker, E. J. W., (1979). Clustering of cations in amphiboles. *Physics and Chemistry of Minerals*, 4, 1-10.
- Wignall, J. W. G., (1966). Mössbauer line broadening in trivalent iron compounds. *Journal of Chemical Physics*, 44, 2462-2469.
- Wilkins, R. W. T., (1968). The hydroxyl-stretching region of the biotite mica spectrum. *Mineralogical Magazine*, 36, 325-333.
- Wilkins, R. W. T., and Ito, J., (1967). Infrared spectra of some synthetic talcs. *American Mineralogist*, 52, 1649-1661.

Manuscript received, February 25, 1982;
accepted for publication, October 8, 1982.