MINERALOGICAL NOTES

The 3d Levels of Ferrous Ions in Silicate Garnets

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Abstract

By considering Mössbauer data for ferrous ions in almandine, an unambiguous choice can be made between the two different models (White and Moore, 1972; Runciman and Sengupta, 1974) recently proposed for the five 3d levels of ferrous ions in almandine. Based on the quadrupole splitting value and its temperature dependence, the model of White and Moore (1972) is definitely favored. The Mössbauer data indicate that the separation of the two lowest levels is about 1100 cm⁻¹. This value enables considerably more precise estimates to be made of the crystal-field parameter and the crystal-field stabilization energy.

Introduction

Two models have recently been proposed for the five 3d energy levels of ferrous ions in silicate garnets which differ quite markedly. The model of White and Moore (1972) was based on descent of symmetry arguments, while the more recent model of Runciman and Sengupta (1974) was based on theoretical treatment of the ferrous site in garnet using a point-charge calculation. These two models differ basically in the energy of the lowest excited state with respect to the ground state: White and Moore (1972) require that the separation between these two states be less than 2000 cm⁻¹, whereas Runciman and Sengupta (1974) require that this separation be about 4500 cm⁻¹.

It is the purpose of this communication to examine these two models for the ferrous ion in almandine and to introduce further evidence into this problem, which favors, unequivocally, the model of White and Moore (1972). The additional evidence comes from Mössbauer quadrupole splitting data for the ferrous site in almandine.

The Two Models

(a) The Model of White and Moore (1972)

Based on the geometry of the ferrous site in almandine described by Novak and Gibbs (1971) and on detailed absorption spectral measurements, White and Moore (1972) suggested the following energies for the five 3d levels in Fe²⁺:

\[
\begin{align*}
{d_{xx}} & \sim 7700 \text{ cm}^{-1} \\
{t_{2g}} & \sim 5900 \\
{d_{x^2-y^2}} & \sim 4350 \\
{e_{g}} & < 2000 \\
{d_{z^2}} & 0
\end{align*}
\]

Although White and Moore were unable to locate the exact position of the \( d_{xy} \) level, they were able to show that the data of Clark (1957) were in error. Clark (1957) had previously claimed finding a spectral band in almandine around 3000 cm⁻¹, but White and Moore failed to find this band. In addition, White and Moore suggested that the calculations of the crystal-field splitting parameter, \( \Delta_c \), and crystal-field stabilization energy, CFSE, carried out by Burns (1970) were in error because such calculations were based on Clark's erroneous data.

The data and model of White and Moore (1972) appeared to resolve a number of problems concerning the optical absorption spectrum of ferrous ions in almandine; however by failing to locate the lowest energy band, their calculated values for CFSE were minimum values and were estimated to be too low by up to 300 cm⁻¹. In addition the observed bands in the almandine spectrum violated the group-theoretical selection rules for direct electronic transitions, since
the band at 4350 cm\(^{-1}\) should not have been observed according to the energy level scheme proposed by White and Moore. Based on the temperature-dependence of the intensities of the bands, these authors showed that vibronic coupling was probably responsible for the relaxation of the selection rules and the observation of all spectral features, including the band at 4350 cm\(^{-1}\).

(b) The Model of Runciman and Sengupta (1974)

In an attempt to interpret the intensity data of the optical absorption spectra of almandine without resorting to vibronic coupling, Runciman and Sengupta (1974) proposed a different model for the ferrous site in almandine based on a quantitative point-charge approach. This type of calculation based only on the nearest neighbor oxygen anions reproduced the energy level scheme proposed by White and Moore (1972). However, by adding two silicon cations of the next coordination sphere into their calculation, Runciman and Sengupta were able to explain the intensity data with the following energy level scheme:

\[
\begin{align*}
    d_{zz} &\sim 7800 \text{ cm}^{-1} \\
    (d_{xy}) &\sim 7000 \\
    d_{xx} &\sim 6000 \\
    d_{yy} &\sim 4500 \\
    d_{zz} &\sim 0
\end{align*}
\]

The band at 7000 cm\(^{-1}\) would not be observed in the absorption spectrum because it is the transition forbidden by the selection rules. Thus, the three observed bands in the near infrared region are then the three transitions permitted by the selection rules.

Although this scheme appears to explain the intensity data well, it requires a very large splitting of the lower, \(e_g\)-derived levels. This splitting is much larger than that of the \(t_{2g}\) levels which interact more strongly with the ligands. Also, by including ions from outside the first coordination sphere, the simple concepts of \(\Delta_e\) and CFSE in relation to the basic polyhedral units are obscured.

Mössbauer Evidence

The basic distinction between the two models, therefore, is in the separation of the two lowest levels \((d_{zz} \text{ and } d_{xx})\) and evidence relating to the separation of these levels should indicate which model is to be preferred. It has been shown (Ingalls, 1964; Gibb, 1968) that the Mössbauer quadrupole splitting as a function of temperature can be related to such data. Indeed, such an analysis of the ferrous ion in almandine has been presented by Lyubutin and Dodokin (1970).

The value of the ferrous quadrupole splitting is determined by two factors: the valence contribution and the lattice contribution (Ingalls, 1964). The valence contribution is temperature dependent because this contribution is determined by the Boltzmann distribution of the sixth 3d electron (which is of opposite spin to the other five) over the 3d levels. For almandine, only the two lowest levels need be considered because levels above 4000 cm\(^{-1}\) are insignificantly populated (less than 0.5%) at temperatures less than 1000 K. The lattice contribution is usually much smaller than the valence contribution (Ingalls, 1964; Nozik and Kaplan, 1967) and is generally of opposite sign to the valence contribution. It is also temperature-independent, so that allowance for this contribution can be easily made. The most simple expression for the quadrupole splitting, \(QS\), at temperature, \(T\), for the case of ferrous ions in almandine is:

\[
QS(T) = QS(0) + F_{lat}\left(\frac{1 - e^{-\Delta_e/kT}}{1 + e^{-\Delta_e/kT}}\right) - F_{lat}
\]

where \(QS(0)\) is the observed quadrupole splitting (in mm/sec) at 0 K, \(\Delta_e\) is the separation of the two levels, \(k\) is Boltzmann's constant, and \(F_{lat}\) is the lattice contribution (in mm/sec) to the quadrupole splitting. The derivation of this expression, which is based on the model of Ingalls (1964), will be discussed in more detail in a forthcoming paper (Huggins and Burns, in preparation).

Taking this approach and assuming that \(F_{lat} = 0\), Lyubutin and Dodokin (1970) used their quadrupole splitting data as a function of temperature to obtain a value of 1080 cm\(^{-1}\) for the separation of the two lowest levels of ferrous ions in almandine. Subsequently, their data have been reworked (Huggins, 1974) making allowance for non-zero values of \(F_{lat}\). Even with a large and unlikely value of 1 mm/sec for \(F_{lat}\), the separation is only increased to 1200 cm\(^{-1}\) and a value of 1100 ± 50 cm\(^{-1}\) appears to be the best fit to the data, allowing for a smaller lattice contribution.

The lattice contribution is assumed to be very small, since at low temperatures (0-300 K) values of the quadrupole splitting for ferrous iron in almandine cluster around 3.50–3.60 mm/sec (Bancroft, Maddock, and Burns, 1967; Lyubutin and Dodokin, 1970; Whipple, 1973). This value is one of the largest quadrupole splittings ever recorded for any ferrous phase.
and suggests that the lattice contribution is quite small.

The value of 1100 cm\(^{-1}\) for the separation of the two lowest levels is clearly at variance with the model of Runciman and Sengupta (1974), but agrees well with the predictions of White and Moore (1972). For the model of Runciman and Sengupta to be correct, the quadrupole splitting would have to show no appreciable temperature dependence (less than 0.01 mm/sec) up to at least 1000 K. In actual fact, the quadrupole splitting drops from 3.65 mm/sec at 0 K to 2.70 mm/sec at about 800 K (Lyubutin and Dodokin, 1970). In addition, the model of Runciman and Sengupta implies a very asymmetric distribution of ionic charge about the ferrous ion, which should also give rise to a large value for \(F_{1at}\). Again, the Mössbauer evidence disagrees.

**Discussion**

The most simple treatment of the temperature-dependence of the Mössbauer quadrupole splitting of almandine shows that the separation of the two lowest 3d levels is about 1100 cm\(^{-1}\). Although the garnet composition may affect this value slightly, the similarity of both the optical and Mössbauer spectra of almandines suggests that differences in composition do not produce any really significant changes in the energies and order of the 3d levels in ferrous ions in almandine. Similarly, more complex treatments of the Mössbauer data may also change the value for the separation somewhat, but as will be discussed in more detail later (Huggins and Burns, in preparation), this simple model is probably the most suitable for obtaining information on the lower 3d levels of ferrous iron in silicates.

The location of the lowest ferrous level in almandine cannot be confirmed by optical absorption spectroscopy because the spectral feature associated with this level must be completely hidden by the main garnet Si–O vibrational band at about 1000 cm\(^{-1}\) (Moore, White, and Long, 1971). Such vibrational features are commonly three to four orders of magnitude more intense than these electronic features.

The almandine specimen, Al-51, used by White and Moore (1972) is nearest in composition to that investigated by Lyubutin and Dodokin (1970). Thus, by combining the optical absorption data for this sample and the Mössbauer evidence on the separation of the two lowest levels, values of CFSE and \(\Delta_c\) were calculated for this particular garnet composition. The 3d energy levels and these parameters are shown in Figure 1. The value for CFSE (~11.0

The model of Runciman and Sengupta (1974) does not agree with the Mössbauer data, and the inclusion of silicon cations from the second coordination sphere must be responsible for the difference, as these authors themselves admit that the first coordination sphere is sufficient to generate the model of White and Moore (1972). Other models of crystal-field spectra (Wood and Strens, 1972; Gaffney, 1972) based only on the first coordination sphere have also proved adequate. Finally, the original criticism of White and Moore’s model for the ferrous site in almandine was based on predictions of the intensities of features in the optical absorption spectrum. As Burns (1974) has indicated, theoretical understanding of selection rules and intensities of bands arising from cations in solids is at present inadequate and can be quite misleading.

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References


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