

INTERVALENCE ELECTRON TRANSFER EFFECTS IN THE SPECTRA OF THE MELANITE GARNETS

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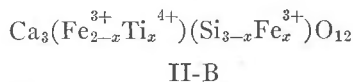
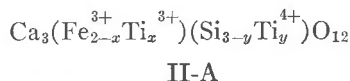
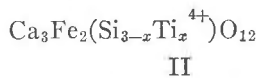
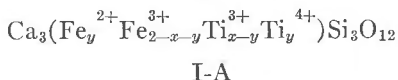
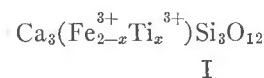
ABSTRACT

New data are presented on the optical spectrum, the infrared spectrum, and the electrical resistivity of the black high-titanium andradite garnets. An evaluation of all available evidence leads to the conclusion that Ti⁴⁺ substitutes on the octahedral site with concurrent substitution of Fe³⁺ and Al³⁺ on the tetrahedral site. The titanium on the octahedral site is mixed Ti³⁺ and Ti⁴⁺ leading to several charge transfer processes which give these garnets their characteristic color and optical spectrum.

INTRODUCTION

The black titanium-rich andradites of the melanite and schorlomite varieties have been the subject of much recent attention. The problem is the role of titanium in the crystal chemistry of these garnets. Among the silicate garnets, most cationic substitution takes place on the cubal or octahedral sites. The tetrahedral site is mainly occupied by silicon. Discrepancies in careful chemical analyses can best be interpreted by assuming the substitution of some other ion, usually Ti⁴⁺, onto the tetrahedral site. There are really two problems: The valence state of the titanium and the sites onto which it substitutes in the structure. The black or brown colors of these garnets also raise questions about the electronic behavior of the titanium. Deep brown and black colors are not easily explained by the usual crystal field spectra of transition metal ions.

The various substitutional possibilities are outlined below. Aluminum is not specifically listed although it also occurs in most titanium garnets.



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Model I assumes substitution of pure Ti^{3+} on the octahedral sites and model I-A mixes the valence states by adjusting the valence state of iron. Chemical analyses which show a clear deficiency in silica and the infrared data both rule heavily against either models I or I-A. Model II and model II-A are the most frequently discussed in the literature. Here Ti^{4+} substitutes on the tetrahedral site with or without concurrent substitution of some Ti^{3+} on the octahedral site. Model II-B is a less discussed alternative which proposes the displacement of Fe^{3+} (or Al^{3+}) to the tetrahedral site and the substitution of Ti^{4+} on the octahedral site. Still more complicated models could be constructed but these will suffice for discussion. There are good chemical analyses which show quite clearly that the SiO_2 content falls short of the required 6 Si per 24 oxygens (Deer, Howie, and Zussman, 1962, and Howie and Woolley, 1968). Microprobe traces across zoned crystals show the variation of iron, titanium, and silicon with each other (Isaacs, 1968; Howie and Woolley, 1968; Gomes, 1969). Phase equilibria (Huckenholz, 1969) and chemical synthesis (Ito and Frondel, 1967) place limits on the extent of titanium substitution.

Other lines of experimentation give direct information on the site distribution and valence state of the ions. Included here are the infrared data of Tarte (1959, 1960, 1965), and Howie and Woolley (1968). Electronic spectra (Manning, 1967, and Manning and Harris, 1970) should yield information on the valence state of the titanium but prove difficult to interpret. Mössbauer measurements give further information on the site distribution of the iron (Dowty and Mark, 1968).

Our purpose in the present paper is to present some new information on the optical spectra and the electrical properties of the high-titanium garnets and to attempt an evaluation and consolidation of the previous work. In addition we make an assessment of the role of delocalized or partially delocalized electrons in explaining the color and spectra of these minerals.

EXPERIMENTAL

The sources for the three garnets examined are given in Table 1. The specimens were checked for phase purity by X-ray and precise diffraction data were measured using an external silicon standard. The lattice parameters were calculated using a least squares method and a Nelson-Riley function. The a values are also tabulated in Table 1. Elemental analyses were determined by emission spectrographic methods. (Table 2) Spectra on all specimens were obtained from finely ground powders by a diffuse reflectance technique using the Beckmann Dk-2A spectrophotometer. An MgO-coated integrating sphere was used with MgO as a reference material. Spectra of polished plate of single crystal by transmission were obtained on the Cary Model 14 spectrophotometer. The temperature dependence of the spectra was determined using a special dewar cell on the Cary at temperatures down to 70°K. Measurements at temperatures above room temperature were made

TABLE 1. ORIGIN, TITANIUM CONTENT, AND CELL EDGE OF HIGH-TITANIUM GARNETS

Sample No.	Origin	Weight percent as TiO ₂	<i>a</i> (Å)
An-Ti 15.20	Ivaarite, Finland	15.20	—
An-Ti 15.45	Magnet Cove, Arkansas	15.45	12.298
An(Ti)-84	San Benito Co., California	6.60	12.101

by heating the specimen with a soldering gun-thermocouple attachment. All high-temperature measurements were made in triplicate to insure reproducibility.

Infrared spectra were measured on powdered samples embedded in KBr using a Perkin-Elmer Model 621 spectrophotometer. Some measurements were made to very low frequencies using powder smears on polyethylene plates on a Beckmann IR-11 spectrophotometer.

The electrical resistivity of a single crystal was measured using a two-point probe arrangement and a standard conductivity bridge.

THE OPTICAL SPECTRUM

Diffuse reflectance spectra are shown in Figure 1 and the single crystal spectrum of the melanite is shown in Figure 2.

Four features appear in these spectra: (i) An intense broad band

TABLE 2. CHEMICAL ANALYSIS OF SPECIMEN ANTI-84

Component	Weight percent
SiO ₂	35.5
Al ₂ O ₃	2.7
Fe ₂ O ₃	19.08
Cr ₂ O ₃	<0.05
FeO	2.22
MgO	1.00
MnO	0.09
CaO	34.5
TiO ₂	6.60
Na ₂ O	0.11
K ₂ O	0.00
Total	101.8

FeO by tritrametric analysis

All other data by emission spectrography

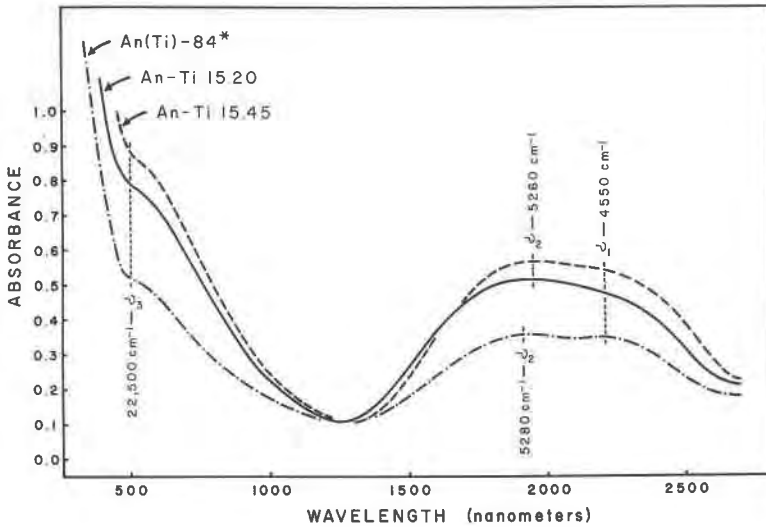


FIG. 1. Diffuse reflectance spectra of titanium-andradite garnets.

occurs in the near infrared at 5280 cm^{-1} . It appears as a broad doublet in the reflectance spectra but only as a single peak in the single crystal transmission spectrum. (ii) All features are superimposed on a very rapid rise in absorption intensity in the blue end of the visible, presumably due to some very intense absorption feature below the observable range. It is this background absorption that gives the garnets their yellow-black

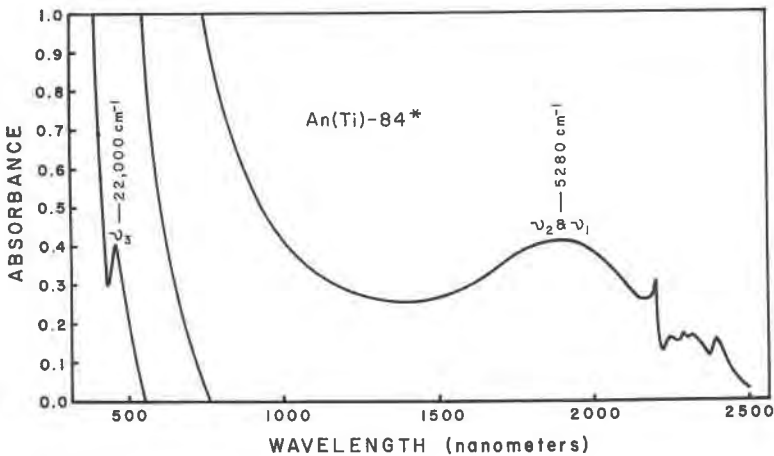


FIG. 2. Transmission spectrum of melanite garnet single crystal. Crystal thickness = 0.24 mm.

colors. (iii) There is a sharp band in the single crystal spectrum superimposed on the intense absorption curve at $22,000\text{ cm}^{-1}$. (iv) There is a broad shoulder at $19,000\text{--}20,000\text{ cm}^{-1}$. The minimum absorbance occurs in the near infrared at 1.2 to 1.4 microns. The positions of these bands agree well with those reported by Manning (1967, 1969).

The intensities of all absorption features are large and obliterate the much weaker spectra of Fe^{3+} and Fe^{2+} . No trace appears of the strongest band of Fe^{2+} in garnet at 7200 cm^{-1} , although this band falls into the most transparent portion of the melanite spectrum. There is also a rough proportionality between the intensity of the absorption features and the titanium concentration. Formal Beer's law plots, however, cannot be drawn because of the difficulty in measuring absolute absorbance from diffuse reflectance spectra and because of the uncertainty in valence state and site distributions.

The temperature dependence of the near infrared band is shown in Figure 3. At low temperatures, the band is clearly resolved into two bands with an unequal temperature response. The behavior of these bands is peculiar if the bands are to be assigned to crystal field transitions. The frequency increases with increasing temperature (Fig. 4) and the intensity decreases (Fig. 5). This is opposite to expectations for

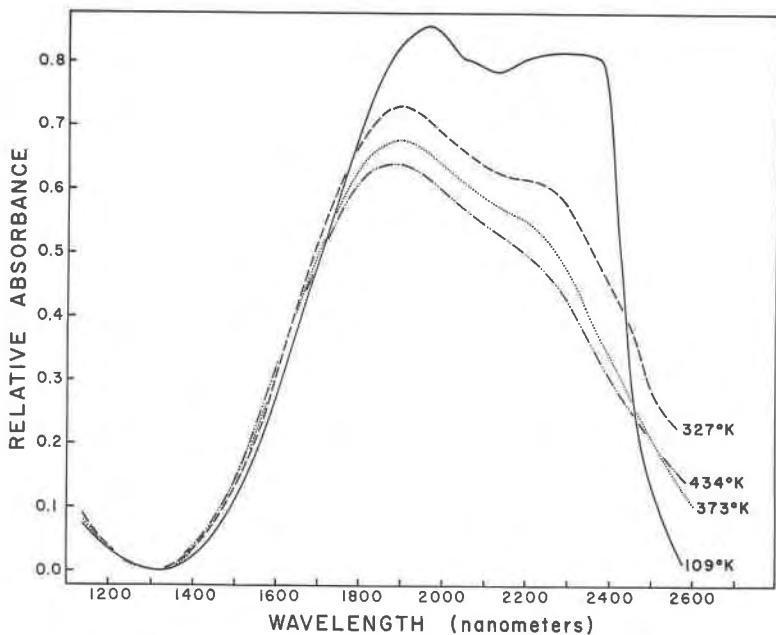


FIG. 3. Effect of temperature on the near-infrared band.

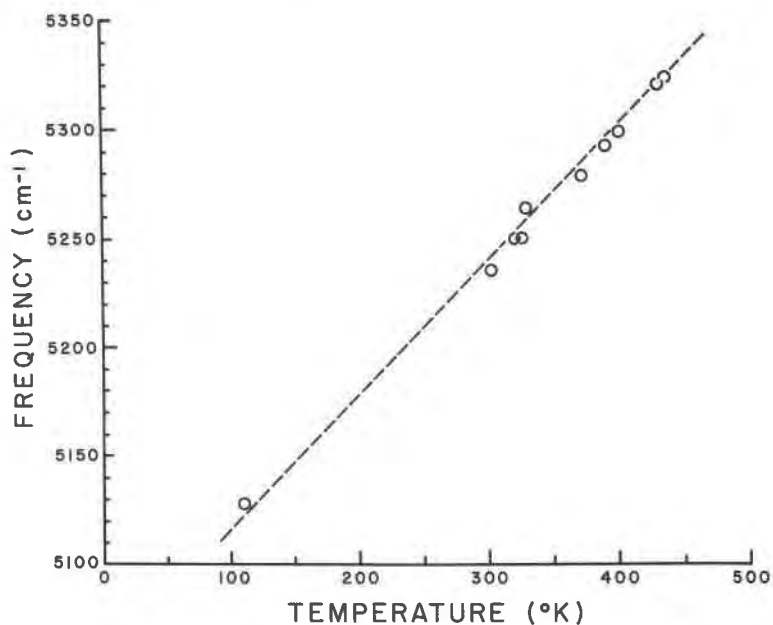


FIG. 4. Variation of frequency of near-infrared band with temperature.

crystal field bands. Crystal field bands would be expected to shift to higher frequencies at low temperature because of lattice contraction increasing the crystal field. Intensities of crystal field bands usually decrease as temperature is lowered. To the contrary, it must be noted

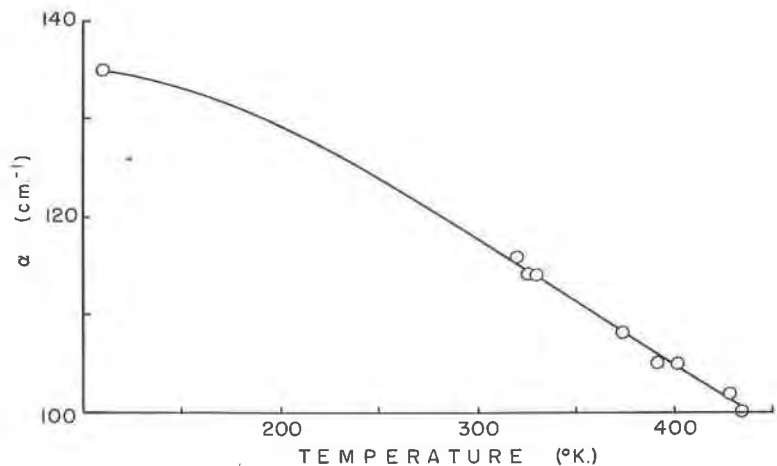


FIG. 5. Variation of intensity of near-infrared band with temperature.

that the half-width of these bands and their intensity are about normal for crystal field bands.

The strong absorption edge in the blue is most likely due to the wing of an intense ligand→metal charge transfer absorption in the ultraviolet. This edge is not present when titanium is absent. It is likewise not present in compounds where the titanium is completely oxidized. The most probable assignment is an $O^{2-} \rightarrow Ti^{3+}$ charge transfer with $O^{2-} \rightarrow (Fe^{3+})^{IV}$ not excluded.

The broad shoulder near $19,000\text{ cm}^{-1}$ was assigned by Manning and Harris (1969) to the ${}^2T_{2g} \rightarrow {}^2E_g$ of Ti^{3+} on the octahedral sites. The sharp band at $22,000\text{ cm}^{-1}$ was said to arise from the ${}^6A_{1g} \rightarrow {}^4A_{1g}$ 4E_g transition of ferric iron. Since all other characteristic Fe^{3+} bands observed in grossularite and andradite are swamped out, some mechanism has to be invoked for the enhanced intensity of this particular transition.

THE INFRARED SPECTRUM

Much of the argument about the site distribution of titanium in melanites and schorlamites has involved the interpretation of the infrared spectra. Tarte (1959, 1960) first published the spectra of a large number of silicate garnets and showed that their spectra were all very similar except for the titanium-rich garnets. The titanium garnets exhibited bands in the 650 cm^{-1} region that were not present when titanium was absent. Tarte interpreted these bands to be the vibrations of TiO_4 tetrahedra. Howie and Woolley (1968) presented IR spectra of a suite of very carefully characterized garnets and came to essentially the same conclusion.

The regions of the spectra of interest for samples An-93, AnTi-84, and An-Ti15.45 are presented in Figure 6. Bands appear at 640 cm^{-1} and 670 cm^{-1} for An-Ti15.45 and at 670 and 738 cm^{-1} for AnTi-84, which are not present in most garnets. In addition, spectra of two aluminum-rich grossularites have an extra band at approximately 750 cm^{-1} and a uvarovite has two extra bands at 675 and 748 cm^{-1} (Moore, White, and Long 1971). The second feature of note is the broadening of the high-frequency tetrahedral bands. The spectrum of sample An-Ti15.20 is nearly identical to that of An-Ti15.45. The bands labeled A, B, C and D in Figure 6 were established as due to stretching vibrations of the SiO_4 tetrahedra. Likewise the low-frequency bands labeled F-L are present in all "normal" garnet structures.

Hurrell *et al.*, (1968) and Moore, White, and Long (1971) have made a theoretical analysis of the garnet structure and have shown that 17 modes are permitted in the infrared. Moore, White, and Long (1971) found all of these can be accounted for in the usual spectra of pyralspites

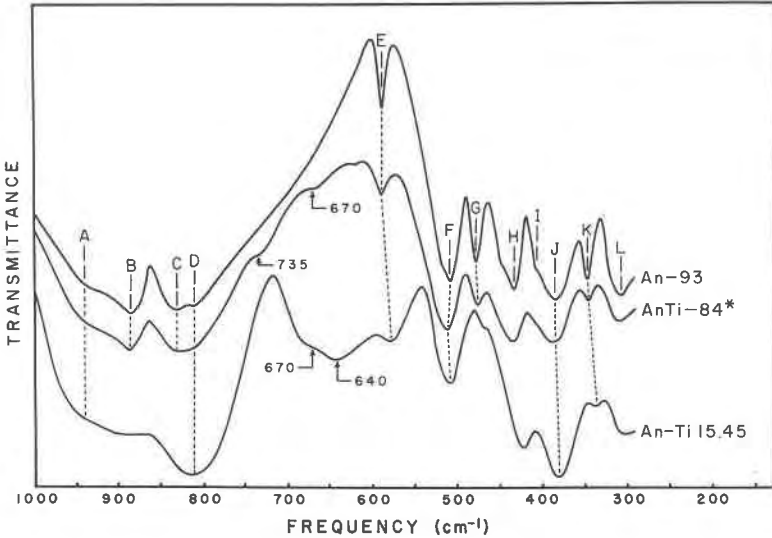


FIG. 6. Infrared spectra of high-titanium garnet in comparison with andradite. Bands marked by letters are the "normal" IR bands of the garnet structure. Bands with labeled frequencies are the "extra" bands.

and ugrandites. The extra bands that appear in Figure 6 are in violation of the garnet space group. The frequency range of these bands leaves little doubt that they arise mainly from the motions of the tetrahedral cations. The evidence that the bands are from TiO_4 tetrahedra seems much more equivocal.

The frequencies of the extra bands and the SiO_4 band of A, B, C and D are plotted as a function of the lattice parameter in Figure 7 (solid circles). The frequencies of the tetrahedral high-frequency bands of yttrium aluminum garnet and yttrium iron garnet (McDevitt, 1969) are also plotted on this figure as open circles. Added for further information are the extra bands from high aluminum grossularite (Gr-92) and a uvarovite (Uv-44).

The extra bands for the high-aluminum garnets Gr-92, Gr-92B, Uv-44 and AnTi-84 do occur in the region of the AlO_4 bands of YAG, while the extra bands of An-Ti15.45 (high-iron and high-titanium garnet) occur in the region of the FeO_4 YIG bands. No analysis of this latter sample was made for Fe_2O_3 , but a sample from Magnet Cove, Arizona (the location of An-Ti15.45) was analyzed by Erickson and Blade in 1963 as reported by Huckenholz (1968). An Fe_2O_3 content of 18.32 wt percent and a TiO_2 content of 15.51 wt percent was found as compared to that reported for sample An-Ti15.45 of 15.45 wt percent TiO_2 . It is probable

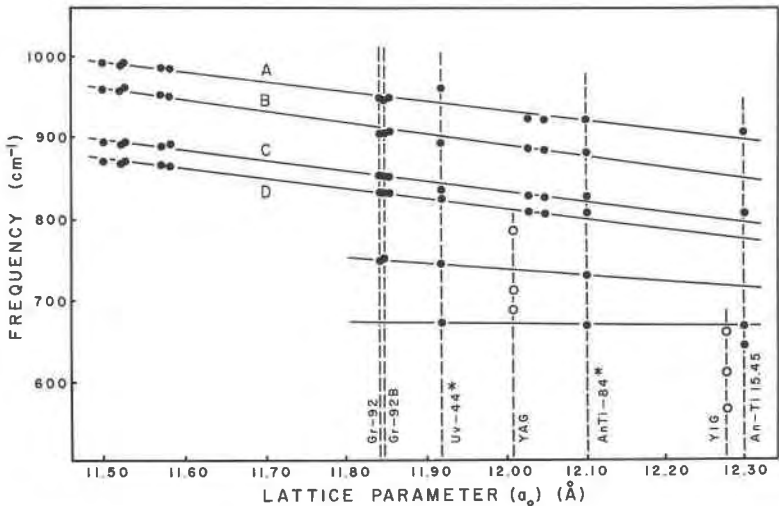


FIG. 7. Frequency versus lattice parameter plot for the extra infrared bands.

that the Fe_2O_3 content of An-Ti15.45 is very close to the value reported by Erickson and Blade for their sample (18.32 wt percent). The Gr-92 and Gr-92B samples only exhibit one extra band and their SiO_4 bands A, B, C, and D are in good linear relationship with the remainder of the natural silicate garnets (Fig. 7). The Uv-44, AnTi-84, and An-Ti15.45 samples have two extra bands and their SiO_4 bands deviate considerably from the linear relation for the same bands established by the other garnets.

The evidence presented implies strongly that both Fe^{3+} and Al^{3+} substitute on the tetrahedral site and give rise to the extra bands in the spectrum. The comparison is directly with known AlO_4 and FeO_4 tetrahedra in the garnet structure and should be valid. Certainly this interpretation is no more arbitrary than was Tarte's assignment of these bands to TiO_4 tetrahedra.

It would be useful to compare the extra bands with spectra of compounds containing isolated TiO_4 tetrahedra. Such compounds are rare. However, numerous spectra of germanium garnets have been reported, mainly by Tarte (1965). The principal stretching region of the GeO_4 tetrahedra is $680\text{--}780\text{ cm}^{-1}$ with the strongest bands at $720\text{--}730\text{ cm}^{-1}$. Since Ge^{4+} has the same charge and is heavier than Ti^{4+} , one would expect the principal stretches of TiO_4 tetrahedra to occur near the frequencies of GeO_4 or slightly higher. It therefore seems less reasonable to assign the bands at $640\text{--}680\text{ cm}^{-1}$ to TiO_4 tetrahedra than it does to assign them to AlO_4 or FeO_4 tetrahedra which because of one less ionic charge have somewhat lower stretching frequencies.

Some comment must be made about the fact that the extra bands occur at all. Theoretically, the substitution of any heavy ion on the silicon site should simply cause the frequencies to shift to lower values. Experimentally, however, some cases are found in which the spectrum of the substituting group appears superimposed on the unperturbed spectrum of the host material. Some specific examples where bands occur in addition to those permitted by the space group are the spinel series $\text{Ni}_2\text{GeO}_4\text{-Ni}_2\text{SiO}_4$ (Tarte and Ringwood, 1962), the mimetite-pyromorphite series (Adler, 1968), and in the substitution of silicon into the tetrahedral site of yttrium iron garnet (Wickersheim, 1960).

The origin of extra bands in the spectra of simple systems with the rock-salt, fluorite, and sphalerite structure is currently a subject of much debate in the physics literature. Several models all based on lattice dynamics, have been proposed. [For three points of view see the papers by Verleur and Barker (1967), Lucovsky and Burstein (1968), and Chang and Mitra (1968).] More complicated structures such as the spinels and garnets have the additional confusion that ordering of cations can also produce extra bands in the infrared spectrum. White and DeAngelis (1967), for example, could explain the multimode behavior of the $\text{Ni}_2\text{SiO}_4\text{-Ni}_2\text{GeO}_4$ spinels by invoking a 1:1 ordering on the tetrahedral sites—although no crystallographic evidence has been forthcoming to prove or reject this explanation.

THE ELECTRICAL PROPERTIES

If electron transfer processes are responsible for the dark colors in the melanite and schorlomite garnets, there should be corresponding changes in the electrical properties. The electrical conductivity of a low-titanium andradite (Titanium = 0.01 wt percent) and of the intermediate titanium-rich andradite, AnTi-84 were measured using a two-point probe and bridge. The room-temperature resistivities were 6.7×10^{11} and 1.3×10^8 ohm-cm respectively. Unfortunately, the crystals of the more titanium-rich garnets were too small for measurement. These data do show that the andradites are insulators and become semiconducting as the titanium concentration increases. The resistivity of AnTi-84 was measured as a function of temperature and the data are plotted in Figure 8. From the slope of the line in Figure 8, the activation energy for charge transfer across the energy barrier can be calculated. The value is 0.47 electron volts or 3800 cm^{-1} . This corresponds rather well to the onset of absorbance in the near infrared band.

DISCUSSION

The Role of Titanium in the Garnet Structure. The various lines of evidence cited can now be pulled together to explain the crystal chemistry of the

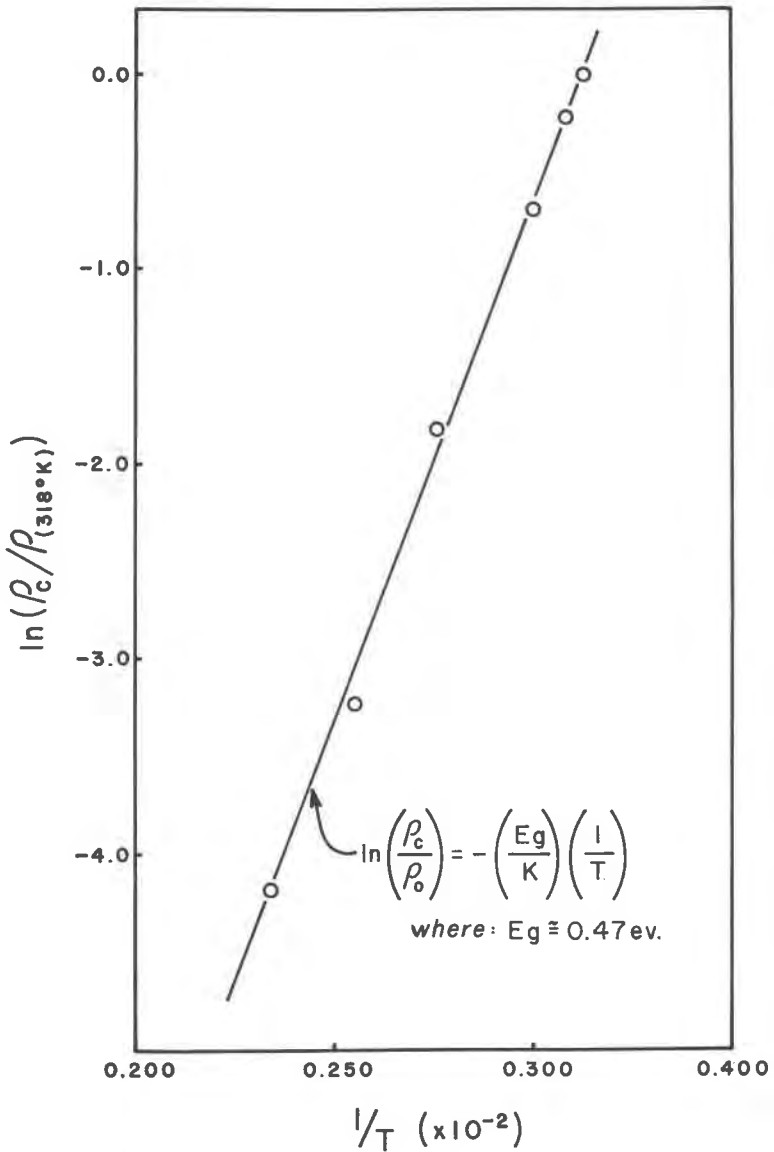


FIG. 8. Variation in the electrical conductivity of AnTi-84 with temperature. The slope gives the activation energy for conduction.

titanium garnets. The evidence that some ion other than silicon substitutes on the tetrahedral site seems overwhelming. The chemical analyses and infrared spectra both require this substitution so all models of Type I can be ruled out. The real argument is between models II and II-A and model II-B. We shall argue the model II-B is the closer approximation.

The only really substantial evidence for 4-coordinated Ti^{4+} has been Tarte's infrared spectra. It was shown in a previous section that the extra bands could be equally well explained by 4-coordinated Al^{3+} and Fe^{3+} and indeed the variation in these bands from one specimen to another suggests that the proportions of tetrahedral substitutions varies.

Also ruling against tetrahedral Ti^{4+} are the crystal chemical arguments recently summarized by Hartmann (1969). Tetrahedral titanium is a crystal chemical rarity whereas tetrahedral aluminum and ferric iron are common. Ito and Frondel (1967) found that they could drive Ti^{4+} onto the tetrahedral sites in synthetic garnets in which the octahedral site was blocked with Zr^{4+} . They were not successful in their attempt to synthesize $\text{Ca}_3\text{Ti}_2(\text{TiFe}_2)\text{O}_{12}$. If Ti^{4+} does not enter the larger FeO_4 tetrahedra, its substitution into the smaller SiO_4 tetrahedra seems unlikely.

The smaller ionic size of Ti^{4+} compared with Fe^{3+} has been cited as evidence that Ti^{4+} should be preferred on the tetrahedral site. It would have been interesting to compare ionic sizes on the new Shannon-Prewitt (1969) ionic radius scale but unfortunately $(\text{Ti}^{4+})^{\text{IV}}$ is so rare that no radius for it is listed.

Evidence that Fe^{3+} occurs on the tetrahedral site is provided by the Mössbauer spectra of Dowty and Mark (1968) who find one type of Fe^{3+} in andradite but two kinds of Fe^{3+} in titanian andradites which they assign to $(\text{Fe}^{3+})^{\text{IV}}$.

The electronic spectra of titanian andradites (Manning, 1967, Manning and Harris, 1970) and work described above are evidence that some titanium is on 6-fold sites and that of this, some is present as Ti^{2+} . Because of the possible charge compensation mechanisms among Fe^{3+} , Fe^{2+} , Ti^{3+} , and Ti^{4+} with resulting enhancement of band intensities by interactions of various kinds, it is difficult to use band intensities to measure the concentration of Ti^{3+} .

In summary the wide variety of experiments that have been performed all seem to indicate that the silica deficiency of the high-titanium garnets is compensated by the substitution of Al^{3+} and Fe^{3+} driven onto the tetrahedral sites by the concurrent substitution of Ti^{4+} on the octahedral sites. The bulk of the titanium seems to go onto the octahedral sites with some unknown portion of it as Ti^{3+} . Of the various measurements, detailed examination of the extra bands in the infrared spectrum would

seem to give the most direct information on tetrahedral site substitutions of specific suites of garnets.

The Electronic Spectrum of Titanium and Charge Transfer Effects. The crystal chemical evidence suggests a mixture of Ti^{4+} , Ti^{3+} , Fe^{3+} , and Fe^{2+} all on the symmetry-equivalent octahedral sites. In this situation the number of possibilities for charge transfer absorption is large and complex.

The yellow-to-black color of titanian andradite arises from an absorption in the ultraviolet and no one has yet measured the band itself. The broad wing extending into the visible is characteristic of ligand→metal charge transfer. Since this absorption wing is at much higher frequencies when only iron is present, we can assume that titanium plays some role.

The sharp band at $22,700\text{ cm}^{-1}$ and the broad shoulder at $19,000\text{ cm}^{-1}$ have been assigned by Manning and Harris (1970) to the ${}^6A_{1g} \rightarrow {}^4A_{1g}$, 4E_g transition of $(Fe^{3+})^{VI}$ and the ${}^2T_{2g} \rightarrow {}^2E_g$ transition of $(Ti^{3+})^{VI}$ respectively. We have nothing further to add to these assignments except to comment that the frequency is in good agreement with the high-intensity $(Fe^{3+})^{IV}$ band in andradite.

The strong double band near 5000 cm^{-1} is difficult to assign. The band shape and intensity favor a crystal field band and if so it is likely due to Fe^{2+} on the tetrahedral sites, as suggested by Manning and Harris (1970). Further evidence for this point of view is the new Mössbauer results of Dowty and Appleman (1970).

An alternative explanation is to assign the band to an intervalence electron transfer transition. $Ti^{3+} \rightarrow Ti^{4+}$ poses difficulties because of the large ($\sim 5\text{ \AA}$) separation of octahedral cations. Another alternative would be $(Fe^{2+})^{VIII} \rightarrow (Ti^{4+})^{VI}$ and many other combinations could be written. Charge transfer involving the tetrahedral cations seems less likely because of the large differences in character between the two sites (Robin and Day, 1967). The intensity of the band would be expected to decrease at low temperature if it were a crystal field band. An increase in intensity would be expected, however, from an intervalence charge transfer band because of the increased orbital overlap at shorter interatomic distances. The frequency of the band is in accord with frequencies observed for many titanium compounds, some of which are listed in Table 3. The frequency of the $Ti^{3+} \rightarrow Ti^{4+}$ interaction is very variable and indeed in the titanium oxides the band varies from $5,500\text{ cm}^{-1}$ in reduced rutile through intermediate values for the Magneli phase, Ti_nO_{2n-1} , series of compounds to $22,000\text{ cm}^{-1}$ for pure Ti_2O_3 (Porter, 1965). The factors that control the frequency of this band are not yet known. The best evidence of the charge transfer origin of this band is the close agreement between the onset of absorption and the activation energy for conduction. Several recent papers (Manning, 1969a, Manning, 1969b, Faye and

TABLE 3. OBSERVATIONS OF NEAR-INFRARED OPTICAL ABSORPTION IN Ti^{3+} -CONTAINING OXIDES

Compound	Near-ir band (cm^{-1})	Reference
Reduced rutile TiO_{2-x}	6700	Johnson <i>et al.</i> , (1968)
Magneli phases Ti_nO_{2n-1}	12,000–15,000 depending on n	Porter (1965)
$SrTiO_{3-x}$	4500	McCarthy <i>et al.</i> , (1969b)
$SrSm_{1-x}Ti_xO_3$	6500–12,000 depending on x	McCarthy <i>et al.</i> , (1969a)

Harris, 1969) have assigned bands in the neighborhood of 20,000–22,000 cm^{-1} in various micas, in andalusite, and in tourmaline to a $Ti^{3+} \rightarrow Ti^{4+}$ electron transfer process.

It would thus appear that the optical and electrical properties of the titanian garnets are dominated by charge transfer effects. These arise because of the mixture of valence states of ions that occupy the octahedral and perhaps cubal sites. The possibility of tetrahedral Fe^{2+} cannot be ruled out on the basis of the electronic spectra.

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