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LOW-TEMPERATURE OPTICAL ABSORPTION AND MÖSSBAUER SPECTRA OF STAUROLITE AND SPINEL

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ABSTRACT

The optical absorption and Mössbauer spectra of natural spinel, synthetic $FeAl_2O_4$ and staurolite have been examined at room and low temperatures for contributions to the spectra from octahedral Fe^{2+}. The major details of the spectra are due to tetrahedrally coordinated Fe^{2+}. The assignment of the peak at $\approx$ 10700 cm^{-1} in the optical spectrum of natural spinel has a temperature dependence in accord with the assignment of this peak to the $^5T_{2g} \rightarrow {}^5E_g$ transition of octahedral Fe^{2+}. The Mössbauer spectra of the natural spinel contain no evidence of octahedral Fe^{2+} but the spectra of $FeAl_2O_4$ measured at 77K or below show a small doublet with a quadrupole splitting of $\sim$1.9mm/sec, which is assigned to Fe^{2+} in a octahedral site with a negative trigonal splitting. Neither type of spectra of staurolite gives clear evidence of octahedral Fe^{2+} though Mössbauer spectra at 4.2K show magnetic ordering and peak intensity variations indicating a distribution of Fe^{2+} cations.

SOMMAIRE

L'absorption optique et les spectres Mössbauer du spinelle naturel, du $FeAl_2O_4$ synthétique et de la staurolite ont été examinés à basse température ainsi qu'à température ordinaire afin de déceler la contribution du Fe^{2+} octaédrique. Les traits principaux des spectres proviennent du Fe^{2+} coordonné tétraédriquement. L'attribution du pic $\approx$10700 cm^{-1} du spectre optique du spinelle naturel dépend de la température, conformément à l'attribution de ce pic à la transition $^5T_{2g} \rightarrow {}^5E_g$ du Fe^{2+} octaédrique. Les spectres Mössbauer du spinelle naturel n'apportent aucune preuve de l'existence de Fe^{2+} octaédrique, mais les spectres du $FeAl_2O_4$, mesurés à 77K ou moins, montrent un petit doublet avec dédoublement quadripolaire de $\sim$1.9 mm/sec, qui est attribué au Fe^{2+} sur site octaédrique avec dédoublement négatif trigonal. Aucun des types de spectres de la staurolite ne prouve la présence de Fe^{2+} octaédrique, bien que les spectres Mössbauer à 4.2K indiquent une mise en ordre magnétique et des variations de l'intensité des pics indiquent une distribution des cations Fe^{2+}.

(Traduit par le journal)

INTRODUCTION

Tetrahedral Fe^{2+} in large concentrations is not commonly found in minerals. The two most well-known examples are spinel ($Mg_{1-x}Fe_xAl_2O_4$) and staurolite. Although both minerals are reputed to contain some octahedral Fe^{2+}, the contributions of these ions to the spectra have not been clearly determined.

Neutron diffraction studies of synthetic $FeAl_2O_4$ show 15% of the Fe^{2+} is in the octahedral Al site (Roth 1964) but the Mössbauer spectra of this spinel have been interpreted as due to tetrahedral Fe^{2+} alone (Ono *et al.* 1966; Rossiter 1965). The room-temperature optical absorption spectra of natural spinels containing Fe^{2+} have been variously interpreted as having only tetrahedral Fe^{2+} (Slack 1964) or reinterpreted as having some octahedral Fe^{2+} (Gaffney 1973; Mao & Bell 1975).

Elucidation of the details of the composition and structure of staurolite has been a particularly difficult problem. In most studies of staurolite, room-temperature Mössbauer spectra are used to argue that the majority of the iron is Fe^{2+} and that the iron is distributed amongst tetrahedral and octahedral sites in the approximate ratio 3/1. Similar spectra and analyses have been given by Bancroft *et al.* (1967), Smith (1968) and Takeuchi *et al.* (1972). However, as the peaks assigned to octahedral Fe^{2+} in the room-temperature spectra merge into the peaks due to tetrahedral Fe^{2+} in the 77K spectra, Dowty (1972) concluded that all the iron is tetrahedrally coordinated. However, as the crystal chemistry evidence (Griffen & Ribbe 1973) suggests that octahedral Fe^{2+} is present in staurolite, there is the possibility that these ions have a lower than usual isomer shift and give peaks in the same position as the tetrahedral Fe^{2+}. For example, the isomer shift of octahedral Fe^{2+} in FeO at 295K is 0.89 mm/sec (Greenwood & Howe 1972), whereas the centre of the staurolite spectrum at 295K is 0.98 mm/sec (Dowty 1972). However, the room-temperature polarized absorption spectra of a staurolite from Pizzo

Forno, Switzerland, have been reported (Bancroft & Burns 1967) and show only a band centred at 6000 cm^{-1} due to the $^5E \rightarrow {}^5T_2$ transition of tetrahedral Fe^{2+}.

We report here an examination of the Mössbauer and optical absorption spectra of spinel and staurolite using low temperatures in an attempt to resolve the conflicting interpretations.

EXPERIMENTAL DETAILS

The spinel samples used in this study were a natural blue crystal and synthetic $FeAl_2O_4$ powder. Analysis of the natural spinel by electron microprobe gave the composition $Mg_{0.918}Fe_{0.072}Al_{2.0067}O_4$, assuming all the iron is Fe^{2+}. The chromium oxide content was less than the detection limit of 0.08 wt. %.

The $FeAl_2O_4$ was prepared from analar grade alumina and ferric oxide by heating at 1040°C for several periods of up to 40 hours under a H_2 and CO_2 atmosphere calculated to give an oxygen partial pressure of 10^{-12} atmospheres. No phase other than $FeAl_2O_4$ was detected in X-ray powder patterns.

The staurolite samples are detailed in Table 1.

The optical absorption spectra were measured using a Cary 17 spectrophotometer over the range 6000 to 31000 cm^{-1}. The low-temperature spectra were obtained using the flow tube technique. Temperatures could be maintained and measured to ±2°K.

TABLE 1. DETAILS OF STAUROLITE SAMPLES.*

A. Brown crystalline in quartz-sericite-schist from Pizzo-Forno, Tessin, Switzerland (sample R20704, Bureau of Mineral Resources, Canberra):
$Fe_{3.15}Al_{17.68}Mg_{0.88}Ti_{0.09}Si_{7.62}O_{44}(OH)_4$

B. Reddish-brown porous in quartz-muscovite-biotite matrix, from Thackaringa, N.S.W.
$Fe_{3.36}Al_{17.76}Mg_{0.62}Ti_{0.11}Zn_{0.05}Si_{7.55}O_{44}(OH)_4$

C. Dark brown twinned porphyroblasts from Mount Isa, N.S.W.
$Fe_{3.62}Al_{17.68}Mg_{0.68}Ti_{0.11}Zn_{0.025}Si_{7.47}O_{44}(OH)_4$

D. Dark brown twinned porphyroblasts from Taos County, New Mexico, Not analyzed.

*Formulae are calculated on a basis of 44(O) + 4(OH).

The Mössbauer spectra were obtained with a constant acceleration spectrometer using a 30mC source of ^{57}Co in Pd matrix. The velocity was calibrated against an iron foil absorber and zero velocity was taken as the centre of that spectrum. Spectra at low temperatures were taken with the sample on a variable temperature insert in a helium dewar. Most of the Mössbauer spectra obtained in this study contained broad peaks and were not amenable to conventional least-squares fitting with either normal or gaussian-broadened Lorentzian lineshapes. Instead, the spectra were analyzed as a distribution of quadrupole splittings about a common centre by a linear least-squares fit to a trigonometric series (Window 1971), and further approximated as a sum of two or three gaussian distributions.

SPINEL

Optical study

The spectrum obtained of a natural spinel crystal at 295K (Fig. 1) is similar to that presented by Slack (1964) for a blue spinel with 2.4% Fe. Cooling the crystal to 47K leads to a general decrease in intensity in the near-infrared and visible producing a number of sharp bands. The decrease results primarily from the temperature variation of the high energy edge of the tetrahedral Fe^{2+} spin-allowed $^5E \rightarrow {}^5T_2$ absorption centred at ~4500 cm^{-1} (Slack 1964; Slack *et al.* 1965) and the loss of a "hot band" at ~13700 cm^{-1}(b). The steep edge at the ultraviolet end of the spectrum is attributed to oxygen to metal charge-transfer processes.

Previous interpretations of the room-temperature spectra of natural spinels containing Fe^{2+} have been in conflict over the contribution due to chromium ions (Slack 1964; Gaffney 1973). In the sample under study the ratio Fe^{2+}/Cr^{3+} is not less than 50. Any Cr^{3+} ions would be situated in the centrosymmetric octahedral site (Miller 1959). Hence, from considerations of

TABLE 2. DETAILS AND ASSIGNMENTS OF THE ABSORPTION SPECTRA OF THE NATURAL SPINEL.

Observed Band Positions (cm^{-1})					Assignments
Unheated		Heated			
47K	295K	47K	295K		
6727					hydroxyl
7033					
10694	11074	10654		a	$^5T_{2g} \rightarrow {}^5E_g$ (Fe^{2+} oct.)
13716				b	$^5E \rightarrow {}^3T_1({}^3H)$ (hot band)
15475	15135			c	
16220	15803	16014	15817	d	
17029	17314	17401	17353	e	
18117	18047	18025	18001	f	$^5E \rightarrow {}^3T_1({}^3H)$
19790	19782	19863		g	$^5E \rightarrow {}^3A_2({}^3F)$
21058	21016	21201	21198	h	$^5E \rightarrow {}^3T_1({}^3P)$
21962	22000	22183	21957	i	$^5E \rightarrow {}^3E({}^3G)$
26167 26279	26142	26144	26117	j	$^5E \rightarrow {}^3T_1({}^3G)$
27528	27287	27240	27081	k	$^5E \rightarrow {}^3E({}^3D)$

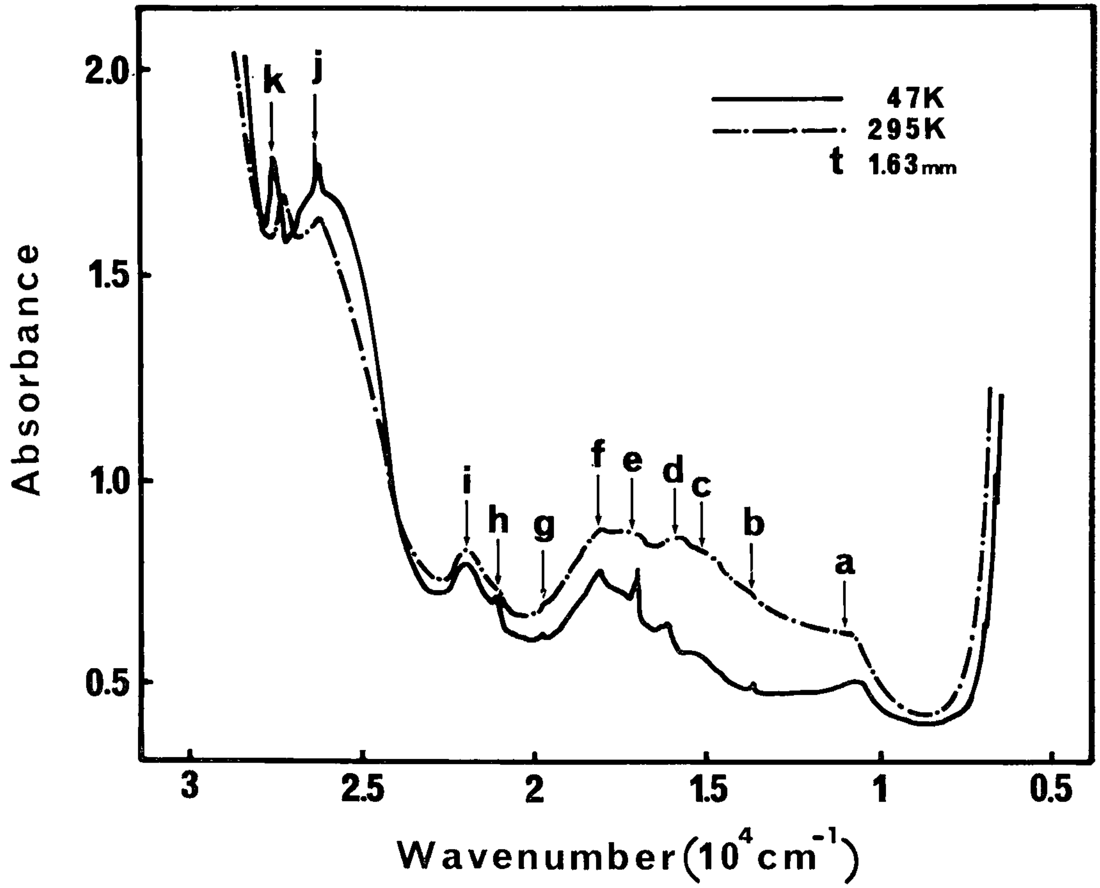

FIG. 1. Optical absorption spectra of the natural spinel crystal taken at 295K and 47K. The crystal thickness (t) was 1.63mm.

cation concentration and site symmetry, the peak intensities of the spin-forbidden transitions due to tetrahedral Fe^{2+} will be at least one and three orders of magnitude greater than Cr^{3+} spin-allowed and spin-forbidden transitions respectively. Thus, all bands in the 18000 to 28000 cm^{-1} energy range are attributed to tetrahedral Fe^{2+} spin-forbidden transitions and have been given assignments (Table 2) closely following those of Gaffney (1973). However, several transitions not reported by Slack (1964) are seen here and have been assigned using the energy level diagram of Marfunin *et al.* (1968) in conjunction with the Racah parameters given by Gaffney (1973). The small splitting of the 26140 cm^{-1} (j) band is attributed to removal of the orbital degeneracy of the $^3T_1(^3G)$ level by either the Jahn-Teller effect or a small distortion in the site symmetry. The sharpening of the bands with decrease in temperature is consistent with these being assigned to spin-forbidden transitions.

The band at ~10700 cm^{-1} (a) shows a temperature dependence in accord with the assignment of this band to the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe^{2+} in an octahedral site (Gaffney 1973; Mao & Bell 1975). This transition has a similar energy in other minerals (Faye 1972) and the decrease in intensity of the band with decrease in temperature is indicative of a forced electric-dipole transition in a centrosymmetric site (Figgis 1966). The lack of splitting in the ^5E_g excited level is also in accord with the D_{3d} symmetry of the octahedral site in spinel.

The presence of octahedral Fe^{2+} introduces some uncertainty into the assignments of the peaks in the 12000 to 18000 cm^{-1} region. The "hot band" at ~13700 cm^{-1} (b) is likely to originate from the tetrahedral Fe^{2+} $^5E \rightarrow {}^3T_1(^3H)$ transition, but, at present, no definite assignment can be given to the peaks at 15475(c), 16220(d) and 17029 cm^{-1}(e). It is difficult to attribute them to the tetrahedral $Fe^{2+}$$^5E \rightarrow {}^3T_1(^3H)$ and

$^5E \rightarrow {}^3E(^3H)$ transitions since this would imply splittings of ~700 cm^{-1} in these transitions and this would be inconsistent with the absence of large splittings in the previous assignments. The energies of the bands are consistent with lower lying (in energy) spin-forbidden transitions of octahedral Fe^{3+} and Fe^{2+} (Manning 1972) but their intensities would seem to be too large relative to the 10700 cm^{-1}(a) band for either type of assignment. It is concluded that although, from the analysis of the sample, it seems reasonable to attribute the origin of the peaks in the 12000 to 18000 cm^{-1} region to iron, only a precise survey of several spinels with varying transition metal ion concentrations covering a wide range of site distributions and valence states could positively determine the correct assignments for these bands.

The optical spectra at 295 and 47K of the natural spinel, after it had been annealed under the same conditions used to produce FeAl$_2$O$_4$, are given in Figure 2. The heating has resulted in a decrease in the intensity of the bands in the 12000-28000 cm^{-1} region and caused a slight increase in intensity of the 10700 cm^{-1}(a) band. The 295K spectrum no longer shows sharp bands. However, in the 12000-28000 cm^{-1} region the peaks occur in the same position as in the spectrum of unheated spinel, and are assigned to the same transitions. The differences in intensity between the spectra is probably due to a difference in tetrahedral site symmetry caused by heating.

As before, the 10700 cm^{-1}(a) band is assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition of Fe^{2+} in the octahedral site and the temperature dependence of the band has changed to be more characteristic of a spin-allowed transition of an ion in a noncentrosymmetric site. We are unable to determine if the amount of octahedral Fe^{2+} increased after the heat treatment as the decrease in symmetry of the octahedral site could alone account for the small increase in intensity of this band between the two 295K spectra.

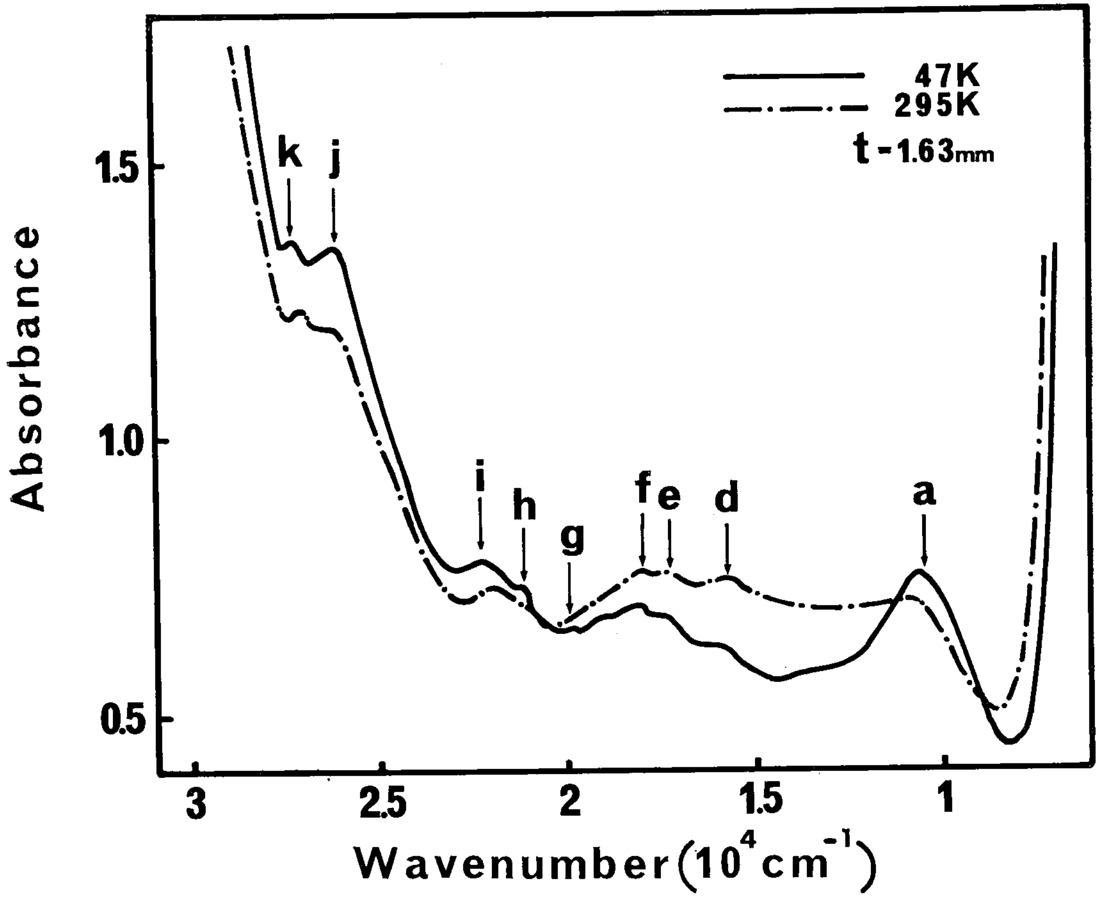

FIG. 2. Optical absorption spectra of the annealed natural spinel taken at 295K and 47K.

Mössbauer study

The natural spinel was investigated at 295, 77 and 4.2K (Fig. 3). The spectra obtained are very similar to those previously published by Ono *et al.* (1967) for a natural spinel containing 2.4% Fe^{2+}. The single peak at room temperature may be assigned to Fe^{2+} ions in a nearly perfect tetrahedral site, but the temperature dependence of the spectra shows there to be small distortions around the Fe^{2+} ions. Such distortions lift the orbital degeneracy of the Fe^{2+} ground state ^5E doublet. In the absence of spin-orbit coupling, a splitting, δ, leads to a temperature-dependent quadrupole splitting (qs) which is independent of the wave function of the ground state of the Fe^{2+} ion and is given by (Gerard *et al.* 1971):

$$qs_T = qs_o \tanh (\delta/2kT).$$

The zero temperature qs_o can be estimated from the spectrum at 4.2K as 3.05 mm/sec. Assuming all the ions to have the same isomer shift and the same value of qs_o, the distribution in qs in the spectrum at 77K could be approximated as three gaussian distributions about δ = 20, 60 and 120 cm^{-1} with relative areas of 58, 14 and 28% respectively.

The distribution in values of δ may be related to the variation in number of nearest Fe^{2+} neighbors around each ion. An ion in a tetradral site has four nearest-neighbor tetrahedral sites at 3.38Å and, for a concentration of 7.4% Fe^{2+} ions randomly distributed in the Mg sites, the probabilities of 0, 1 or 2 nearest Fe^{2+} ions are 74, 23 and 2.7% respectively. The effect of next-nearest neighbors and inversion of Mg and Al ions will cause a broadening of the δ values, but the figures show the main distortions in the natural spinel may be related to nearest-neighbor distributions.

The spectra taken of the annealed spinel (Fig. 4) show that the heating has considerably changed the environment of the Fe^{2+} ions. The broad peaks are centred about 0.89 mm/sec., indicating the Fe^{2+} is still tetrahedrally coordinated. A "mean" qs splitting of the two peaks yields a value of 205 cm^{-1} for the splitting of the ^5E level but the broad peaks indicate a wide distribution of splittings about this value.

The 295K spectrum of synthetic $FeAl_2O_4$ (Fig. 5) is very similar to that of the annealed spinel as has been previously reported (Ono *et al.* 1966), except that some asymmetry is seen

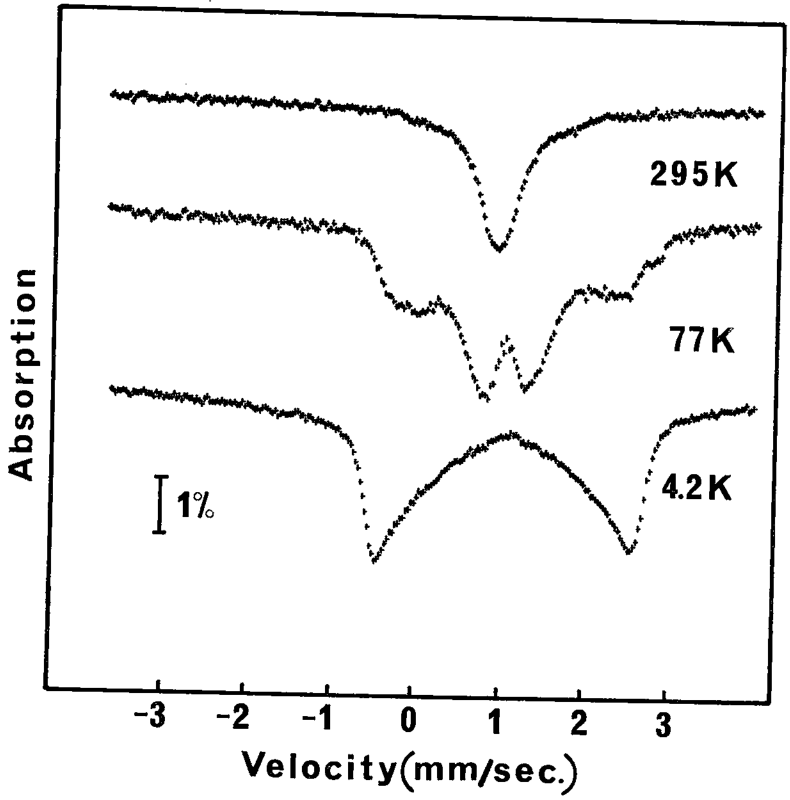

FIG. 3. Mössbauer spectra of the natural spinel.

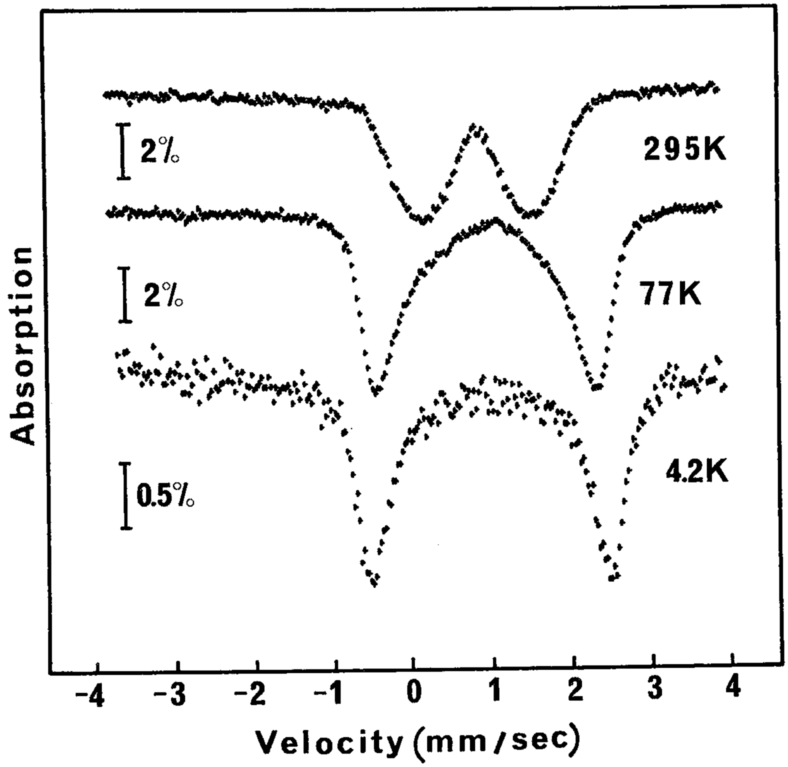

Fig. 4. Mössbauer spectra of the annealed natural spinel.

in the peaks. Cooling the sample to 77K and 26.5K reveals two prominent shoulders at 0.3 and 1.9 mm/sec. Spectra at lower temperatures contain broadened lines as a result of magnetic ordering. Previous spectra of FeAl$_2$O$_4$ at low temperatures have been analyzed as one broadened doublet (Ono *et al.* 1966). However, the two shoulders can be assigned to a doublet due to octahedrally coordinated Fe^{2+}. Accurate values of the isomer shift and *qs* of this inner doublet could not be obtained as the outer lines still show considerable asymmetric broadening, but at 26.5K the values are estimated as 1.2 and 1.9 mm/sec., respectively.

The assignment of a small *qs* to octahedral Fe^{2+} is consistent with the trigonal symmetry of that site in spinel. In a trigonally distorted octahedral field the T_{2g} ground state is split into an orbital doublet ($\psi_{\pm1}$) and a singlet (ψ_0) level. The value of *qs* is determined by whether $\psi_{\pm1}$ or ψ_0 is the ground state and by their separation. The two $\psi_{\pm1}$ levels give contributions to the electric field gradient of $\frac{2}{7}e\langle r^{-3}\rangle$, or a value of *qs* of up to 2 mm/sec. The singlet ψ_0 gives a contribution of $-\frac{4}{7}e\langle r^{-3}\rangle$ (Ono & Ito 1964). Fe^{2+} ions in an inverse spinel such as GeFe$_2$O$_4$ show a large *qs* of $\simeq$3.0 mm/sec. at a low temperature, consistent with a singlet ground state (Varret & Imbert 1974). In such a spinel the oxygen parameter $u = \frac{3}{8}$ and the oxygen polyhedron is octahedral. A positive trigonal field arises from six neighboring Al^{3+} ions at 2.88Å with a trigonal angle of 35.26°. In a normal spinel, the large divalent ion in the tetrahedral site results in an increase in *u* to 0.387 for MgAl$_2$O$_4$ (Wyckoff 1965) and $u = 0.3885$ for FeAl$_2$O$_4$ (Roth 1964), and causes an expansion of the oxygen octahedron along the trigonal axis. If the negative trigonal field of the oxygen ions is greater than the positive field of the Al^{3+} ions, the doublet becomes ground state and the *qs* will have a maximum value of around 2 mm/sec.

The crystal field due to the oxygen ions should dominate the effect of more distant ions and the inner doublet in the spectra of the synthetic spinel is assigned to octahedral Fe^{2+}. The broad lines of the higher temperature spectra prevent the temperature dependence of *qs* of the octahedral Fe^{2+} being obtained and hence no estimate of the trigonal splitting if the $^5T_{2g}$ level can be made. The broadened lines in the low-temperature spectra also prevent an accurate de-

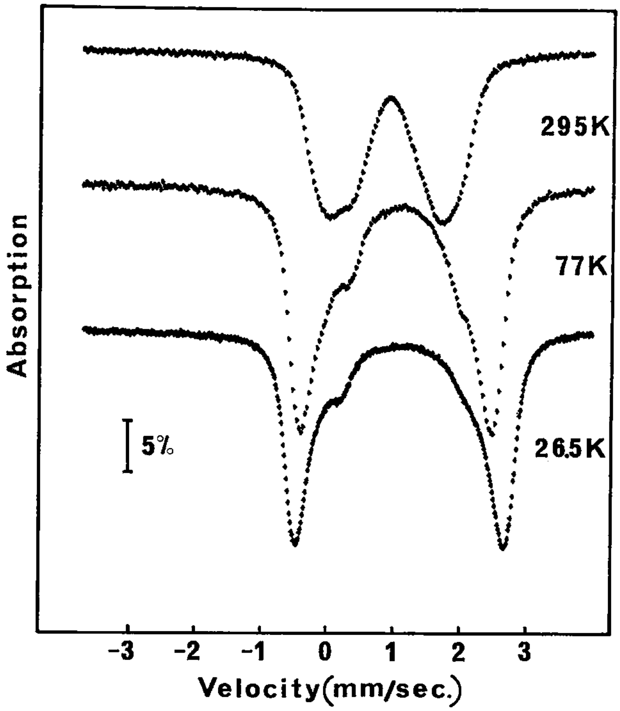

FIG. 5. Mössbauer spectra of the synthetic $FeAl_2O_4$.

termination of the degree of inversion in the $FeAl_2O_4$ sample. Area measurement, after approximating the shape of the low-velocity peaks, yields a figure of 15%, which is of the same order as that obtained by neutron diffraction (Roth 1964).

Having identified the position of the peaks from octahedral Fe^{2+}, the spectra of the natural spinel were examined closely for evidence of octahedral iron. The 295K spectrum of unheated spinel does show slightly asymmetric wings which could be due to a very small contribution from octahedral Fe^{2+} but the broad peaks of the tetrahedral Fe^{2+} prevent any definite detection of octahedral Fe^{2+} in either the natural or annealed spinel. A final comment on the two-doublet room-temperature spectrum reported by Yagnik & Mathur (1968) for synthetic spinel needs to be made. We were unable to reproduce that spectrum, which differs from both the spectra of our synthetic $FeAl_2O_4$ and of the heated natural spinel, and as shown above, a *qs* of 2.76 mm/sec is not expected for octahedral Fe^{2+} in a normal spinel.

Fe^{2+} ions in the octahedral sites in other normal spinels should also exhibit the doublet ground state. Octahedral Fe^{2+} in Fe_2TiO_4 were proposed to have such a ground state to account for the high anisotropy of the magnetic susceptibility of Fe_2TiO_4, but the Mössbauer spectrum of these ions could not be resolved from the broad spectrum of the tetrahedral Fe^{2+} (Banerjee *et al.* 1967). Similarly, the normal spinel FeV_2O_4 has broadened lines which mask any doublet of the size predicted for octahedral Fe^{2+} (Ono *et al.* 1968).

STAUROLITE

Optical study

We have re-examined the absorption spectra at 46K of the Pizzo Forno staurolite (Table 1) in the expectation that the major transitions of both octahedral and tetrahedral Fe^{2+} will give sharper bands at the lower temperature, as with spinel. However, the spectra obtained at 46K were the same as obtained by Bancroft & Burns (1967) at 295K, and there were no features in the 10000 cm^{-1} region. The experiment is inconclusive as to observe a band some 100 times weaker than the 6000 cm^{-1} band of the tetrahedral Fe^{2+} requires a thick sample. When a staurolite crystal with a thickness of 1 mm was used, the 10000 cm^{-1} region was "swamped" by the tail of the very intense oxygen to metal charge-transfer band.

Mössbauer study

The Mössbauer spectra of the four samples of staurolite were examined over the temperature range 20-550K and showed no features that could be used to confirm the presence of octahedral Fe^{2+} in staurolite. The spectra taken at 4.2K (Fig. 6) show magnetic ordering and it is on this we will concentrate. The four samples give similar spectra in that the peaks are in similar positions and extensively broadened, though of unequal intensities. The Mössbauer spectrum at 4.2K of synthetic $FeAl_2O_4$ is also shown. The broad lines in the five spectra are indicative of a range in the magnitude and orientation of the magnetic and quadrupolar interactions as a result of the random cation arrangement. Such spectra are difficult to analyze in detail because of the similar magnitudes of the magnetic and quadrupole interactions for Fe^{2+} and the need to specify relative orientations.

However, a comparison may be made between the origin of ordering in $FeAl_2O_4$ and staurolite, since a similarity exists between spinel and the arrangement of the major octahedra and tetrahedra in the "iron" layer in staurolite as shown in Figure 7 (Hollister 1970). The analogy is approximate as the symmetry and occupancies of the polyhedra vary in staurolite and in particular the Al octahedra have C_s rather than the D_{3d} symmetry of spinel.

The magnetic exchange between tetrahedral ions in spinel could be by direct exchange, though the distance of 3.5Å to the four nearest tetrahedral neighbors would make the exchange small. However, the ordering temperature of 8K for $FeAl_2O_4$ (Roth 1964) implies that only small exchange energies are involved. Other exchange

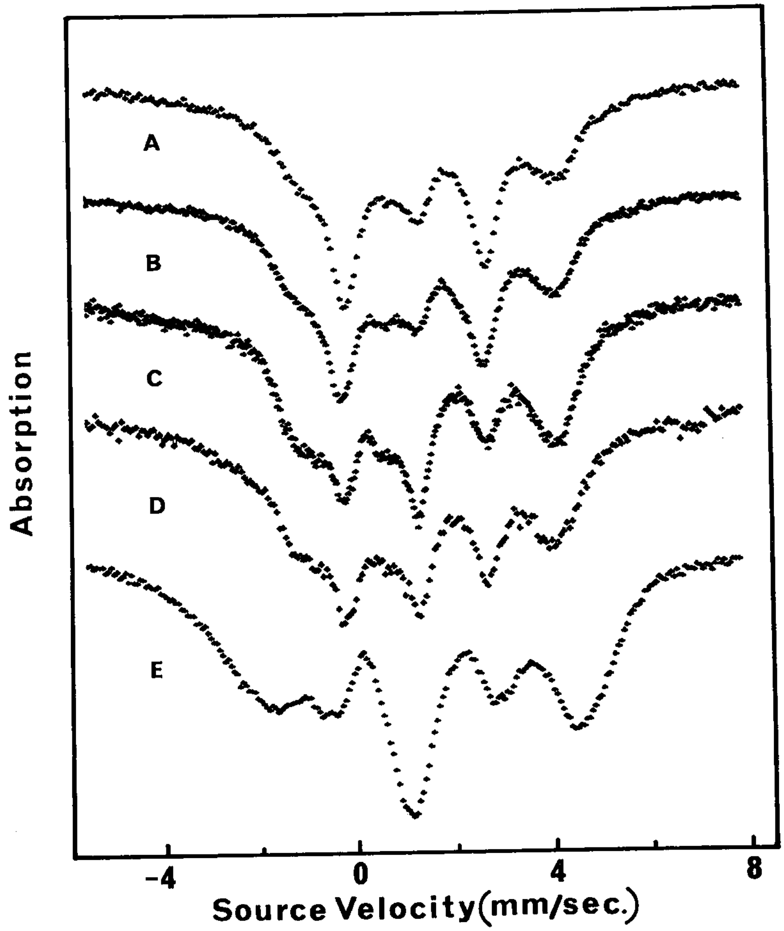

FIG. 6. Mössbauer spectra at 4.2K of the four staurolite samples and of the synthetic $FeAl_2O_4$ (E). Spectra labels A to D refer to details of the staurolite samples given in Table 1.

mechanisms such as super–superexchange via two anions (Goodenough 1963), or via empty orbitals of the Al^{3+} ions (Roth 1964) could play some role. Neutron diffraction studies of $FeAl_2O_4$ show no long-range ordering at 4.2K, whereas the normal spinels $CoAl_2O_4$ and $MnAl_2O_4$ do order at 6K and 4K respectively (Roth 1964). The difference was attributed to the strong superexchange between tetrahedral and octahedral Fe^{2+} ions as a result of the small inversion in $FeAl_2O_4$.

With staurolite there are considerably fewer pathways for magnetic exchange apart from the direct exchange mechanism, yet an ordering temperature of 7 ± 1K was found for the sample B staurolite. This could indicate Fe^{2+} in octahedral sites in the "iron" layer giving strong superexchange with tetrahedral Fe^{2+}. However, the shorter separation of each tetrahedral ion from its two neighbors (3.31Å and 3.29Å) could also lead to increased direct exchange. The uncertainty in site symmetry in these sites precludes quantitative estimates of the direct exchange energy. However, the variation of the peak intensities in the spectra of the four staurolites does suggest variations in the distribution of the Fe^{2+} ions, since all four have similar iron concentrations. This could relate to the conditions of formation and paragenetic details of the particular sample. The two samples from New Mexico and Mount Isa had similar form and gave similar spectra, whereas the other two samples, which also gave similar spectra, were both in micaceous matrices. A distribution of Fe^{2+} is only possible if the iron occupies octahedral as well as tetrahedral sites. Thus, although the evidence is not conclusive, it is suggested that the inner peaks in the room-temperature staurolite spectra with isomer shifts and quadrupole splittings in the ranges 0.98 to 1.03 mm/sec. and 1.25 to 1.56 mm/sec., respectively (Dowty 1972) are due to octahedral rather than tetrahedral iron.

Conclusion

For spinel, the contribution from octahedral Fe^{2+} in the low-temperature optical absorption and Mössbauer spectra has been demonstrated. The Mössbauer spectrum of these ions has a quadrupole splitting of less than 2 mm/sec. due to the negative trigonal field giving a doublet ground state. The position and temperature dependence of the band at 10700 cm^{-1} enable assignment to the $^5T_{2g} \rightarrow {}^5E_g$ transition of the octahedral Fe^{2+} ions.

With staurolite, we have been unable to reach any firm conclusion regarding the presence of

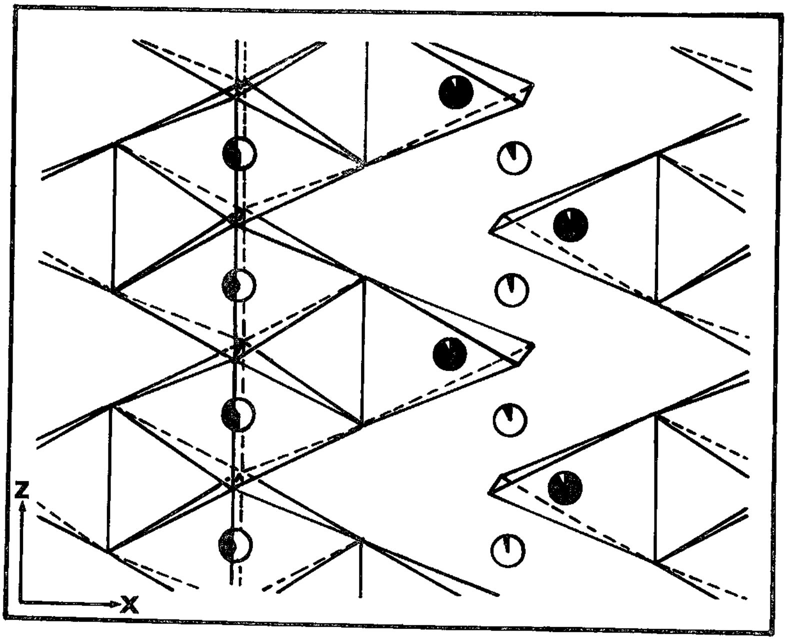

Fig. 7. Schematic drawing of the $Al_{0.7}Fe_2O_4$ ("iron layer") of staurolite showing arrangement of Fe tetrahedra and Al octahedra. Approximate site occupancies as determined by Smith (1968) are indicated by filled portions of circles.

octahedral Fe^{2+}, though the sample dependence of the Mössbauer spectra at 4.2K do indicate some distribution of the Fe^{2+} ions.

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