

⁵⁷Fe NGR of Fe Phases in “Magnetic Cassiterites”

I. Crystal Chemistry of Dodecahedral Fe²⁺ in Pyralspite Garnets

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Abstract. A pyralspite garnet from an anomalously magnetic concentrate of a pegmatitic cassiterite ore has been investigated using ⁵⁷Fe nuclear gamma-ray resonance spectroscopy. The quadrupole splitting and isomer shift values of 3.6 mm/s and 1.4 mm/s, respectively, are among the largest observed for Fe²⁺ ions and indicate a very low covalency of the dodecahedral Fe²⁺–O²⁻ bonds. These data support the more recent and lower value (10.2–10.1 kcal/mole) of White and Moore (1972) for the CFSE of the dodecahedral Fe²⁺ ion and suggest that the CFSE should be a useful approximation to the site preference energy of Fe²⁺ for this site.

1. Introduction

As a part of a systematic investigation of the origin of the magnetism in natural cassiterites (Grubb and Hannaford, 1966), a specimen of cassiterite concentrate from the Kamativi tin mines in Rhodesia was obtained for ⁵⁷Fe Mössbauer measurements. This particular specimen was chosen because it was reported to have anomalous magnetic properties (Grubb, 1973).

It has been suggested that the magnetism of some cassiterites obtained from pegmatites (Ramdohr, 1961) is due to FeTa₂O₆ exsolution from columbites. It is known, however, that FeTa₂O₆ is not magnetically ordered at ambient temperatures (Evans, 1975); on the other hand, there is little doubt that the FeTa₂O₆ inclusions in cassiterite can account fully for its being designated a “magnetic cassiterite.” This apparent contradiction results from the large susceptibility of pure, paramagnetic phases such as FeTa₂O₆ relative to that of a cassiterite fragment that contains only about 0.1 weight percent of a magnetically ordered phase such as Fe₃O₄. This becomes immediately obvious when one considers, for example, the magnitudes of the initial permeability of Fe₃O₄ and the susceptibility of FeCO₃. Pure FeCO₃ has a susceptibility of 1×10^{-3} emu/g and a fragment of cassiterite that contains 0.1 weight percent of Fe₃O₄ would also have an initial permeability of only about 1×10^{-3} emu/g. Thus, it is possible to have mineral species in the magnetic fractions of cassiterites that are purely paramagnetic phases. We wish to report on such a phase that we have found in some cassiterite concentrates from the Kamativi Mines in Rhodesia.

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After additional magnetic separation of an ore concentrate on a Frantz Isodynamic magnetic separator, a transparent pale-pink phase was found to be concentrated among the “*magnetic*” fractions being separated at low field strengths. Further, it was possible to lift with a small permanent magnet 0.5 mm fragments of this pink phase. From the less than 50 mg of this pink phase that was obtained, samples were prepared for X-ray diffraction analyses, qualitative electron microprobe analysis, wet chemical analysis and ^{57}Fe Mössbauer analysis.

Early in our analyses, the pink phase was determined to be a pyralspite garnet and it was decided to continue the analyses since there are very little data on the Fe^{2+} ion in the dodecahedral site of garnets and further since there is some interest in the crystal chemistry of this site in terms of site preference and crystal field stabilization energies. Thus far, only four ^{57}Fe Mössbauer or nuclear gamma-ray resonance (NGR) investigations of garnets containing dodecahedral Fe^{2+} ions have been reported (Marfunin *et al.*, 1967; Bancroft, Maddock, and Burns, 1967; Prandl and Wagner, 1971; Lyubutin and Dodokin, 1971). In these studies, however, the garnets investigated contained little or no manganese, and it is of interest to see what effect the manganese ion has on the crystal chemistry of the dodecahedral site as revealed by the ^{57}Fe hyperfine interaction parameters.

In agreement with other studies, we obtained values for the electric quadrupole coupling constant and the isomer shift that are simultaneously among the largest observed for a Fe^{2+} ion. The close approach of the quadrupole coupling to the maximum value of 4.8 mm/s expected for a single, occupied d-orbital outside of the symmetric, half-filled d^5 configuration indicates significant asymmetry in the charge distribution of the dodecahedral sites in these silicate garnets. The large isomer shift also suggests a small degree of covalency consistent with the large electric quadrupole splitting (Hazony, Axtmann, and Hurley, 1968), internuclear separation and volume associated with this site (Novak and Gibb, 1971). This interpretation of the ^{57}Fe NGR hyperfine parameters has important crystal chemical implications for the bonding in garnet structure materials.

2. Experimental

Because of the small amount of material available, some significant modifications in techniques were necessary at certain stages of the analysis. The pink garnet phase was separated from the cassiterite ore concentrate using a Frantz Isodynamic magnetic separator; this separation was very incomplete and the garnet phase was finally separated as a pure phase by hand picking. Each fragment was about 0.3 to 0.5 mm on an edge, was of a uniform color; and all fragments were of the same pale pink color.

Qualitative electron microprobe analyses were performed using a semiconductor detector and 1024 channel analyzer and indicated the presence of Si, Al, Mg, Ca, Mn and Fe. Analyses were performed for a number of different fragments and all gave the same relative intensities of the peaks of the different elements, suggesting a negligibly small variation in the composition of the fragments. Wet microchemical analyses were performed for all of the elements whose presence was indicated in the qualitative electron microprobe analyses. The results of these analyses in weight percentages are MnO 6.06, FeO 29.30, SiO_2 31.77, Al_2O_3 21.46, CaO 1.0 and MgO 1.44. X-ray diffraction analyses were performed using the Debye-Scherrer method, with a 114.6 mm diameter camera and a Straumanis film placement with Mn filtered $\text{FeK}\alpha$ radiation. The lattice constant

was deduced from α_1, α_2 split doublets in the back reflection region and found to be $11.538 \pm 0.003 \text{ \AA}$. The refractive index, n_D , was determined to be 1.791.

Because of the small sample size, special arrangements were necessary for obtaining acceptable ^{57}Fe NGR spectra. A sample of approximately 2 mm in diameter was prepared from garnet fragments which had a total mass of approximately 13 mg. The sample was placed in a graded (Al-Pb-Brass) shield/collimator with a 2 mm diameter hole. A special 25 mCi Co^{57}/Rh source with a 1 mm diameter active area was also employed. The source-absorber-counter assembly was mounted on a lathe-bed type optical bench and accurately aligned with precision x-y translators. Except for these modifications, the typical "time-mode" method of data collection was employed (Evans, 1968) utilizing an electromechanical transducer with a sawtooth velocity waveform and 512 channels of a 1024 channel analyzer. All spectra were obtained with source and absorber at 298 K. The spectra were analyzed using least-squares fitting techniques described previously (Evans, Ghose and Hafner, 1967).

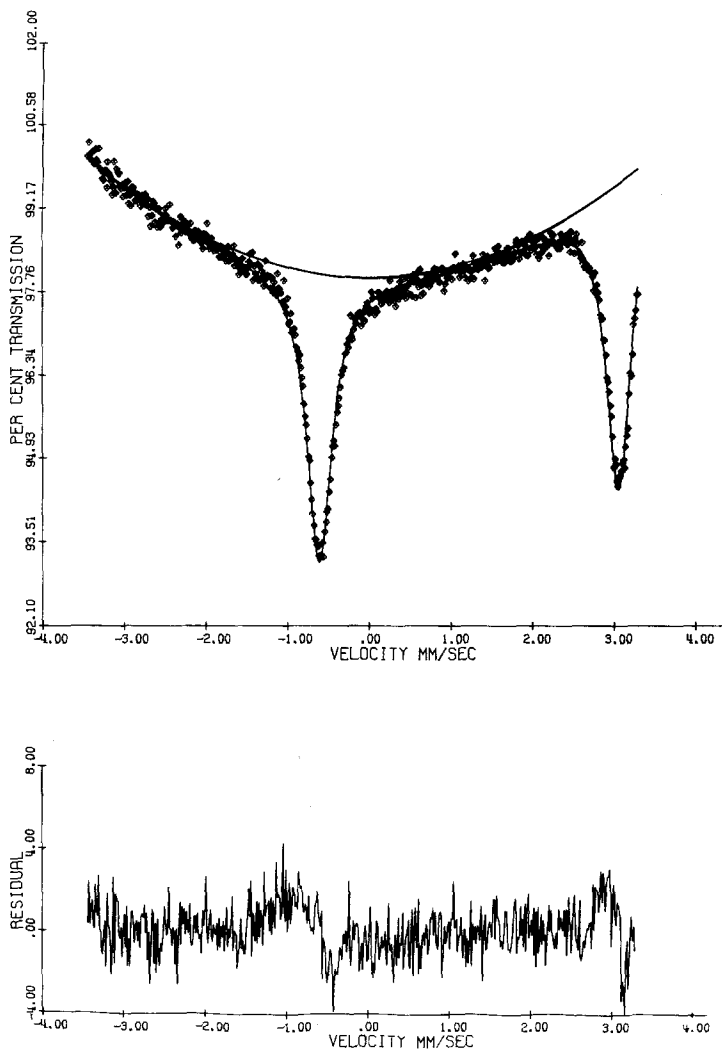


Fig. 1. ^{57}Fe NGR spectrum of pyrralspite garnet at 298 K. The lower graph is the difference between the experimental data, the points, and a fit (solid line) of two lorentzian lines to the data

3. Results

A typical ^{57}Fe NGR spectrum of the pyralspite garnet is shown in Fig. 1a. Different fragments all give identical spectra. The points are the experimental data and the solid line is the result of fitting two independent, lorentzian-shaped lines to the spectrum. The difference between the experimental data and the fitted spectrum is illustrated in Fig. 1b, as the “*Residual*”; the magnitude and randomness of the excursions across the zero line is a measure of the quality of the fit. These two lorentzian-shaped lines provide a good fit to the data; and the small linewidths indicate that the fit is probably unique. A spectrum obtained over a large velocity range shows the absence of any magnetically ordered phase. The NGR parameters are given in Table 1.

4. Discussion

4.1. Spectral Features

Two significant aspects of the ^{57}Fe NGR data of this garnet are: (1) the occurrence of a single oxidation state of Fe, e.g. Fe^{2+} , on a single lattice site; and (2) the rather extreme values for the isomer shift and electric quadrupole interaction.

Table 1. ^{57}Fe NGR Parameters for dodecahedral Fe^{2+} ion in garnets

Garnet ^a Composition	Temperature (°K)	Isomer shift ^b (mm/s)	Quadrupole Splitting (mm/s)	Linewidth Γ (mm/s)
Almandine ^c	300	1.25	3.60	^d
Andradite ^c	300	1.39	3.70	^d
	80	1.40	3.73	^d
Pyrope-Almandine 20% Fe^{2+e}	300	1.30	3.56	0.41 ^f
Pyrope-Almandine 69% Fe^{2+e}	300	1.30	3.53	0.40 ^f
Almandine ^g	300	1.29	3.49	0.33 ^h
	77	1.50	3.69	0.83 ^h
Almandine ⁱ	300	1.20	3.55	^j
	77	1.44	3.68	^j
Pyralspite ^k	300	1.28	3.57	0.31 ^l

^a Minor and trace elements are not included in these compositions.

^b Relative to Fe-metal absorber.

^d Marfunin *et al.* (1967).

^f Bancroft, Burns, and Stone (1967).

^h Prandl (1971).

ⁱ Lyubutin and Dodokin (1971).

^l Γ is 0.334 ± 0.006 mm/s for the low velocity line and 0.300 ± 0.007 mm/s for the high velocity line. The integrated area ratio, $\text{Area}_{\text{low velocity}}/\text{Area}_{\text{high velocity}}$, is 1.088.

^c No composition data available.

^e Only composition data available.

^g $\text{Ca}_{0.36}\text{Fe}_{1.83}\text{Mg}_{1.04}\text{Al}_{1.72}\text{Si}_{3.05}\text{O}_{12}$

ⁱ $\text{Fe}_{2.60}\text{Mg}_{0.57}\text{Al}_{1.99}\text{Si}_{2.84}\text{O}_{12}$

^k See text for composition.

That the major pattern in the NGR spectrum of the pyralspite garnet is derived from Fe^{2+} at a single crystallographic site is deduced from (1) the magnitudes of the linewidths relative to those of calibration standards in which Fe is known to occupy a single lattice site and (2) the symmetry of the areas, widths, and intensities of the absorption lines. The average linewidth of 0.33 mm/s is somewhat larger than the 0.25–0.28 mm/s (without corrections for thickness and instrumental effects) expected for a pattern resulting from a single crystallographic species. The broadening of the lines results, however, from thickness effects and self-absorption in the source; and the width of the lines for the garnet spectrum is the same as that for a sodium nitroprusside calibration standard and for the inner lines of a Fe metal standard absorber obtained using the same 1 mm diameter active area 25 mCi Co^{57}/Rh source.

4.2. Quadrupole Interaction and Isomer Shift

In terms of the bonding and electrostatic interactions in the garnet structure, it is of considerable interest that the asymmetry of the Fe^{2+} pattern so characteristic of the NGR spectra of silicates with different cations on the same lattice site (Evans, Ghose, and Hafner, 1967; Virgo and Hafner, 1969) is absent in this garnet. This indicates that the bonding and electrostatic interactions between the Fe^{2+} ions on the dodecahedral site and the ions in other dodecahedral sites and in the tetrahedral and octahedral sites are relatively insensitive to variations in either the *oxidation number* or *electronic structure* of these ions. The relative insensitivity of the NGR parameters of the dodecahedral Fe^{2+} ion to the differences in the bonding at other cation sites certainly results to some extent from the high coordination number, large number of polyhedral elements, and the consequent, small influence that changes in a small number of these elements has on the electronic structure of the dodecahedral Fe^{2+} ion. As will be shown below, however, a full understanding of these results require a *qualitative* difference in the bonding at the dodecahedral site compared to the octahedral and tetrahedral sites.

The unusually large values of *both* the isomer shift and quadrupole interaction are convincing evidence that the local electronic structure and bonding properties of the Fe^{2+} ion are the primary determinants of these parameters. The quadrupole splitting of the dodecahedral site Fe^{2+} ion in garnets is among the largest observed and approaches the maximum expected value of 4.8 mm/s for a completely ionic Fe^{2+} ion. The value of the electric quadrupole splitting is somewhat larger than that in other silicates inasmuch as the ground state of a d^6 ion is non-degenerate, i.e., an orbital singlet, in the D_2 symmetry appropriate to the dodecahedral site in garnets.

The lifting of the degeneracy of the 3d levels as result of the crystalline potential of D_2 symmetry at the dodecahedral site is presented in Fig. 2.

The quadrupole splitting may be related to pertinent crystal chemical parameters through the following relationship (Ingalls, 1964):

$$\Delta E = (2/7) e^2 Q(1-R) \langle r^{-3} \rangle F(\Delta_1, \Delta_2, \lambda, T) + \Delta E_{\text{lattice}} \quad (1)$$

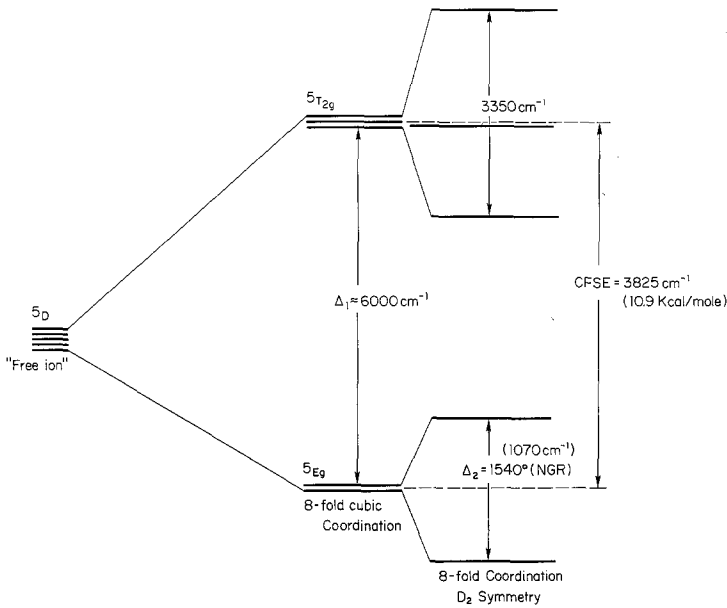


Fig. 2. Splitting diagram for the 5D term of the Fe^{2+} ion in eight-fold coordination, corresponding to a cube or square prism and the garnet dodecahedral site with D_2 symmetry. The splitting Δ_2 of the lower two levels was obtained from temperature dependent NGR measurements (Lyubutin and Dodokin, 1971); the splitting of the upper three levels was taken from White and Moore (White and Moore, 1972)

where e is the magnitude of the charge on the electron; Q is the electric quadrupole moment of the ${}^{57}\text{Fe}$ nucleus; $(1-R)$ is the antishielding factor for the valence electrons; $\langle r^{-3} \rangle$ is the average value of the inverse cube of the radial extent of the d orbitals; and $F(\Delta_1, \Delta_2, \lambda, T)$ depends on the details of the crystalline potential, and of the electronic structure of the ion, i.e., Δ_1 and Δ_2 are level separation parameters indicated in Fig. 2, and λ is the spin-orbit coupling constant. Δ_1 is about 1540 K (Lyubutin and Dodokin, 1971) and λ is about 150 K (Ingalls, 1964). In fact the spin-orbit coupling parameter for Fe^{2+} in the dodecahedral site of a garnet is not known and the value of 150 K is that of "free" Fe^{2+} ion. If the electric quadrupole splitting is reasonable insensitive to temperature up to 300 K, it is well-established that the effect of spin-orbit coupling on the electric quadrupole interaction will be small compared to the effect of the level splittings Δ_1 and Δ_2 . For dodecahedral Fe^{2+} ions in garnets, the quadrupole splitting changes by only 5 percent between 77 K and 300 K and the differential temperature effect of $F(\Delta_1, \Delta_2, \lambda, T)$ is negligible. Since the dodecahedral Fe^{2+} has a singlet ground state, $F=1$ and Eq. (1) becomes

$$\Delta E = (2/7) e^2 Q (1-R) \langle r^{-3} \rangle + \Delta E_{\text{lattice}} \quad (2)$$

The effects of covalency will influence both $(1-R)$ and $\langle r^{-3} \rangle$ but the changes in $\langle r^{-3} \rangle$ are expected to predominate; and a covalency parameter α_c^2 can be

defined such that

$$\alpha_c^2 = \langle r^{-3} \rangle / \langle r^{-3} \rangle_0 \quad (3)$$

where $\langle r^{-3} \rangle_0$ is the value appropriate to a "free" Fe^{2+} ion. We can then define a free ion value for the quadrupole splitting, ΔE_0 , such that

$$\Delta E_0 = (2/7) e^2 Q \langle r^{-3} \rangle_0 (1-R)_0 \quad (4)$$

and Eq. (2) becomes

$$\Delta E = \Delta E_0 \alpha_c^2 + \Delta E_{\text{lattice}} \quad (5)$$

For a properly chosen series of materials in which $F(A_1, A_2, \lambda, T)$, the site symmetry and crystalline field parameters are similar, the variations in the electric quadrupole splitting would reflect primarily variations in the covalency of the Fe^{2+} ion. Convincing application of these ideas has been made by Hazony (Hazony, 1971) for a series of compounds $\text{FeCl}_{6-n}(\text{H}_2\text{O})_n$, where n goes from 0 to 4. The least covalent compounds are those in which Fe^{2+} is octahedrally coordinated by H_2O ; this is as expected on the basis of a wealth of experimental and theoretical data (Johnson, 1967). Despite the fact that similar measurements are not available for eight-fold coordinated Fe^{2+} , the good agreement of the isomer shift-quadrupole splitting correlations for the garnets with that for $\text{FeCl}_{6-n}(\text{H}_2\text{O})_n$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ (Fig. 4) indicates that the effects of the difference in coordination number and spin-orbit coupling constant are small.

The lattice contribution to ΔE is neglected in this discussion because it is either very small or nearly constant for the dodecahedral site as evidenced by the data in Table 1.

Therefore, Eq. (5) is a good approximate description of the electric quadrupole interaction for the dodecahedral Fe^{2+} ion in garnets. The significance of this relationship is that quantitative information on the nature of the chemical bonds at the dodecahedral site can be obtained from a single measurement. We note that the Fe-O bonds at the dodecahedral site are on the average about 75 percent ionic [cf. Eq (5) and Fig. 3] which is considerably higher than that of octahedral Fe-O bonds. This result is in qualitative agreement with an earlier conclusion that the effective nuclear charge on the dodecahedral Fe^{2+} ion is only 10% less than the free ion value (Bloomfield, Lawson, and Rey, 1961).

More recent measurements (Hodges, Dorman, and MaKram, 1969) indicate that Mn^{2+} in the dodecahedral site is about 95 percent ionic. This measure of the ionicity of dodecahedral Mn^{2+} is based on the hyperfine coupling constant, the Pauling electronegativity scale and the assumption of a linear relationship between the two. Using the Pauling electronegativity scale, the precise values for the ionicity of Mn^{2+} and Fe^{2+} with 8-fold oxygen coordination are 93.6 percent and 92.5 percent, respectively. The relative order of ionicities deduced for Fe^{2+} and Mn^{2+} by these rather different techniques is therefore in agreement with electronegativity considerations. The relative magnitudes of the ionicities are, however, in poor agreement. The poor agreement results primarily from an artifact of the Pauling electronegativity scale which frequently leads to overestimates of the ionicity (Phillips, 1973). For example, the ionicities of ZnS and ZnO are calculated using the Pauling scale to be 80 percent and 86 percent

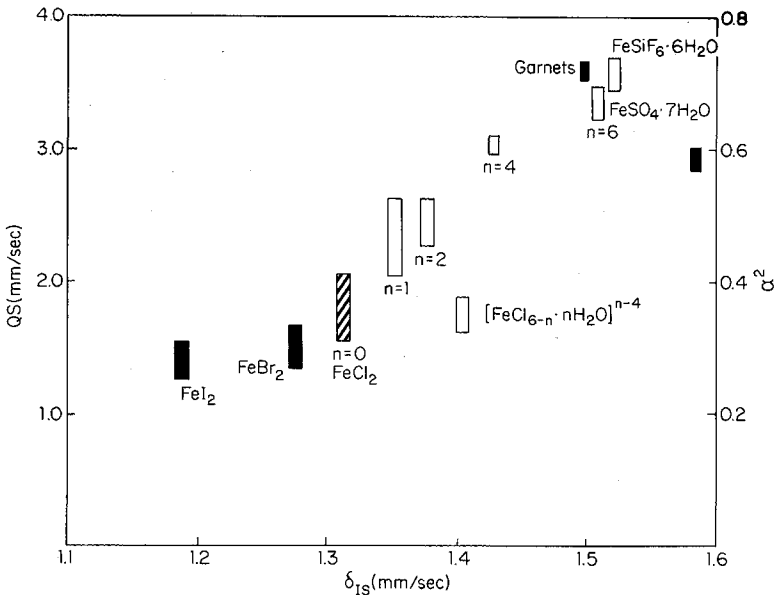


Fig. 3. Quadrupole splitting–isomer shift correlation for octahedral Fe^{2+} from Hazony (Hazony, 1971) with modifications. The bar for the garnets is from this study. The covalency parameter, α^2 , is also plotted on the vertical axis. The height of the bars represents variation in the quadrupole splitting from 90 K to 300 K, and the width of the bars represents the experimental uncertainty in the isomer shift

ionic, respectively, whereas the ionicities calculated using the dielectric scale (Phillips, 1973) are 62 percent and 61 percent, respectively. The dielectric scale of electronegativities has been shown to be superior to Pauling's scale for crystalline materials and we conclude, therefore, that our estimates of 75 percent ionicity for the dodecahedral Fe^{2+} ion is approximately correct and that the 95 percent estimate for the ionicity of Mn^{2+} on the dodecahedral site in garnets is perhaps too high.

4.3. Crystal Field Interactions

The weak covalence of the metal-oxygen bonds for the dodecahedral Fe^{2+} ion has important consequences for the description of the crystal field splitting at this site. Recently, a range of values from 10.2 kcal/mole to 10.7 kcal/mole has been presented by White and Moore (White and Moore, 1972) for the crystal field stabilization energy (*CFSE*) of the dodecahedral Fe^{2+} ion. This new range of values differs somewhat from the earlier estimate of 11.7 kcal/mole to 12.4 kcal/mole advanced by Burns (Burns, 1970). As a result of a reconsideration of the interpretation of the optical spectra of garnets and a new estimate of the cubic crystal field splitting parameter, White and Moore consider their estimate of the *CFSE* to be more accurate than that of Burns. White and Moore (White and Moore, 1972) based their estimate of the *CFSE* on a larger *derived*

value for the cubic crystal field splitting parameter, Δ_c (same as Δ_1 in Fig. 3), and a smaller estimate for the splitting between the ground state E_g levels than those employed by Burns (Burns, 1970). In fact, the ground state splitting parameter, Δ_2 , was assumed to be zero by White and Moore in their calculations; we now know Δ_2 to be 1070 cm^{-1} , Fig. 2 (Lyubutin and Dodokin, 1971). As we shall show below in our analysis of the NGR data and estimate of Δ_c , we, too find a value of 10.3 kcal/mole for the CFSE of the dodecahedral Fe^{2+} ion in good agreement with the conclusions of White and Moore. Our estimate of the CFSE is based, however, on different values of Δ_c and the inclusion of the splitting of the E_g levels; and the agreement of our estimate with that of White and Moore is to some extent fortuitous.

In their analysis, White and Moore used a Δ_c value of 10000 cm^{-1} appropriate to Fe^{2+} in MgO to derive Δ_c for the dodecahedral Fe^{2+} ion in garnets. Correction factors appropriate to a point-ion model were employed, i.e.

$$\Delta_c(\text{garnet}) = (8/9)\Delta_c(\text{MgO}) (r_{\text{Fe-O}})_{\text{garnet}}^5 / (r_{\text{Fe-O}})_{\text{MgO}}^5 \quad (6)$$

where $\Delta_c(\text{MgO})$ is the cubic crystal field splitting parameter in MgO; $8/9$ is the correction factor in going from 6-fold coordination to 8-fold coordination; $(r_{\text{Fe-O}})_{\text{garnet}}$ and $(r_{\text{Fe-O}})_{\text{MgO}}$ are the internuclear Fe—O distances in garnet and MgO, respectively; and $(r_{\text{Fe-O}})_{\text{garnet}}^5 / (r_{\text{Fe-O}})_{\text{MgO}}^5$ is a correction for the different internuclear separations in MgO and garnets and is based on the inverse fifth-power dependence of the crystal field parameter in a point-ion approximation.

This scheme for deriving Δ_c for the pyralspite garnets assumes that the covalency is either negligible or quite similar for Fe^{2+} in MgO and pyralspite garnets. The NGR data for Fe^{2+} in MgO (Chappert *et al.*, 1969) and in the pyralspite garnets, Table 2, indicate considerably more covalency in the Fe—O bonds in MgO than in the garnets; and a reasonable estimate of Δ_c for the dodecahedral Fe^{2+} ion in the garnets from that for octahedral Fe^{2+} in MgO would require adjustments for the different degrees of covalency in addition to those in Equation 6. There are no tractable models that permit semiquantitative adjustments in Δ_c for covalency effects. The effects of differences in covalency on Δ_c should be minimal, however, for octahedrally coordinated Fe^{2+} with bonding parameters that are similar to those of the dodecahedral Fe^{2+} ion in garnet; and application of the corrections in Equation 6 should lead to a Δ_c value in better accord with a larger body of bonding parameters.

As shown in Fig. 3, $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ and $\text{Fe}(\text{F})_6^{4-}$ species in the solid state have bonding properties very similar to those of dodecahedral Fe^{2+} ion in garnets and would be preferred to Fe^{2+} in MgO for arriving at a value of Δ_c for the garnets. A Δ_c value of 10000 cm^{-1} is often quoted for $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ but is believed to be only approximate since this value is derived directly from the optical spectra and the effects of low symmetry crystalline fields have not been taken into account (Holmes and McClure, 1957). On the other hand, the Δ_c value of 7000 cm^{-1} for FeF_2 is known quite accurately (Oelkrug, 1971). We have, therefore, taken the arithmetic average of these two values to obtain a Δ_c for the pyralspite garnets of 5100 cm^{-1} after applying the corrections in Equation 6. The detailed values for the crystal field splitting parameters are shown in Fig. 3. We note that the CFSE is quite similar to that of White and Moore whereas Δ_1 is interme-

diate between the estimates of Burns and of White and Moore. The level splittings in Fig. 3 seem more reasonable than that proposed by White and Moore since the 5900 cm^{-1} transition would require either a zero splitting of the E_g levels, which is known to not be the case (Lyubutin and Dodokin, 1971), or a downward shift of the 5B_3 level by about 500 cm^{-1} , which seems unreasonable. Our level scheme is similar to the proposed in an article by Huggins (Huggins, 1975) which was published after this article was submitted for publication. There are still substantive differences, however, in estimates of some of the splitting values.

4.4. Implications for Garnet Crystal Chemistry and Conclusions

The unusually small covalency of the dodecahedral Fe^{2+} ion in garnets has some far-reaching implications for our understanding of garnet crystal chemistry. Of overall significance is the weak interaction, implied by the low covalency, between the Fe^{2+} ion and the coordinating oxygen ligands. Since the degree of covalent bonding is small, geometrical and point-ion type electrostatic interactions would be the principal determinants of the local crystal chemistry of this site. Thus we have justification for the fact that size considerations determine whether or not a particular ion will occupy this site. Hybridization will not be important for ions on this site.

The small covalence of the dodecahedral site is of greater importance, however, in terms of its implications for bonding at other sites. Namely, the small covalence at the dodecahedral site suggests substantial covalence at the octahedral and tetrahedral sites. In fact, the similarity in the quadrupole splitting-isomer shift values for the dodecahedral Fe^{2+} ions and octahedral Fe^{2+} ions with H_2O ligands suggests that the SiO_4^{4-} tetrahedra can be treated as virtual polyatomic anions with very strong intraspecies bonding and very weak interactions with the Fe^{2+} ion. Since the covalency of the Al-O bonds in the octahedra is also expected to be considerable, the dodecahedral metal-ligand interactions are expected to be weaker for $\text{X}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ silicates compared to $\text{X}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ and $\text{X}_3\text{Y}_2\text{Ge}_3\text{O}_{12}$, for example. Further quantitative support for the appreciable covalence of the Si-O bonds is found in a theoretical study which successfully accounted for a substantial portion (though not all) of the optical spectra of a pyralspite garnet and predicted a covalence of 54% for the Si-O bonds (Bloomfield, Lawson and Rey, 1961). Further, in a study of lattice potentials in silicate garnets which successfully accounted for many of their general and detailed structural features, a charge of 0 was assigned to silicon corresponding to a covalence of 50% (Born and Zemann, 1964).

For a given dodecahedral cation, variations in the local geometry of the dodecahedron are likely to be due primarily to packing and geometrical considerations for the tetrahedral and octahedral coordination polyhedra. Hence, the variations in the lengths of shared versus non-shared edges, of bond lengths and metal-metal distances for the dodecahedral site will be of less significance for bonding considerations in garnets than for the octahedral and tetrahedral sites in other silicates such as spinels, olivines, and pyroxenes. These conclusions are in substantial agreement with a recent analysis of the crystallographic and

coordination polyhedra parameters for garnets (Novak and Gibbs, 1971); and the "stability" field for garnets derived in that study wholly on the basis of geometrical considerations would appear to be consistent with the electron density distributions and chemical bonding. The difference in the chemical bonds of the various cation sites also has important structural implications; and on the basis of the above considerations, it is expected that as the covalence of the tetrahedral site, metal-oxygen bonds decreases, the nature and bonding characteristics of the dodecahedral site cation will become more important in influencing the garnet structural parameters. The "stability" field for non-silicate garnets is likely to be different from that of the silicate garnets.

Lastly, because of the low covalence of the Fe–O bonds at the dodecahedral site, it is expected that the site preference energy of Fe²⁺ for this site is likely to be very close to its CFSE. The available NGR measurements on Fe²⁺ in pyralspite garnets support the more recent range of values of White and Moore (1972) for the CFSE of Fe²⁺ in the dodecahedral site of garnets (Fig. 2).

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