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# EPR-determined site distributions of low concentrations of transition-metal ions in minerals: Review and predictions

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## ABSTRACT

Data for distribution of small concentrations (up to 1% per site) of $Mn^{2+}$, $Fe^{3+}$, $Cr^{3+}$, and $V^{4+}$ among different sites in minerals determined by electron paramagnetic resonance are reviewed. In some cases a decision between controversial site assignments can be made. In cases where only one site is occupied, the results enable one to state qualitative rules for site preferences. Kinetic factors, rather than equilibrium relations, are found to be important in certain cases, but considerably more systematic study is required to allow correlation with the growth conditions or thermal history of a mineral.

## INTRODUCTION

In an interesting review (Hawthorne, 1983), electron paramagnetic resonance (EPR) is listed among the less-developed methods for quantitative determination of site occupancies. However, for most transition metals and for rare earth ions that are present only in small amounts (up to about 1% per site), it still is the most powerful method. That is because this method gives unambiguous information about the valence state and site symmetry, and, at least for some ions, it enables precise determination of geometries (distortions of their first coordination spheres) from characteristics of their EPR spectra. Thus, occasionally, controversial site assignments can be unambiguously determined, provided the crystal structure of the pure host compound is known with sufficient accuracy.

Three areas of increasing complexity are of interest in connection with site distributions of transition-metal ions in minerals: (1) distribution ratios and their variability for minerals from different geochemical environments and with different growth and thermal histories, (2) factors controlling these distributions, namely equilibrium or kinetic factors during crystal growth or changes thereafter, and (3) determination of differences in site distribution energy (in the case of equilibrium distributions or of activation energies), kinetic control during crystal growth, and elucidation of the underlying causes.

The present study concentrated on ions for which sufficient data are available in the literature, namely, $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, and $V^{4+}$. Preference for occupancy of a special site by these ions depends mainly on their nature and surroundings, and it can be constrained in connection with the following considerations.

## SITE PREFERENCE ENERGY

Evidently, the site preference energy (or ligand field stabilization energy, ΔLFSE) for $Cr^{3+}$ (Fig. 1) is so large that it can substitute only in sites of octahedral symmetry. The absence of any site preference energy for the isoelectronic $d^5$ ions, $Mn^{2+}$ and $Fe^{3+}$, in sixfold- or fourfold-coordinated sites suggests that substitution of them is affected by other factors.

The site preference energy of $Cr^{3+}$ favors occupation of Al sixfold-coordinated sites, e.g., in spinels, garnets, and topaz (Burns, 1970; Petrov et al., 1977), as has been known for a long time. Almost exclusive occupation of Al sixfold-coordinated interstitial sites by this ion in berlinite may be ascribed to the same cause. The intrasite partition coefficient $K$ between sixfold- and fourfold-coordinated sites is greater than 100 in favor of interstitial sixfold sites (Henning et al., 1967). Although no EPR spectra were detected for $Cr^{3+}$ for the distorted interstitial octahedral sites, most likely because they were broadened beyond detection by static disorder, the optical absorption spectra can be used for precise site assignment.

In andalusite two crystallographically nonequivalent Al sites are present with sixfold- and fivefold-coordination according to Burnham and Buerger (1961). However, a more recent investigation (Papendick et al., 1988) proposes fourfold- instead of the fivefold-coordination. Since EPR spectra of $Cr^{3+}$ from only one center were observed (Vinokurov et al., 1962; Holuj et al., 1966), $Cr^{3+}$ can be assigned unambiguously to the sixfold-coordinated site, although the differences between distortion from superposition model analysis (SPM) and zero field splitting patterns (ZFS) indicate a pronounced local relaxation around this ion (Buscher et al., 1987). The same combination of Al sites is found in sillimanite (Winter and Ghose, 1979). Again only the sixfold-coordinated site was found to be occupied by $Cr^{3+}$ (Le Marshall et al., 1971).

$Mn^{2+}$ was found to occupy the interstitial sixfold-coordinated sites in berlinite (Behner et al., 1986). Only the central transition of this ion could be observed, indicating a high static disorder, as in the case of $Cr^{3+}$. In addition, the $^{55}Mn$ hyperfine splitting resolved at Q-band frequencies led to the site assignment. Similar results were obtained for $Mn^{2+}$ in quartz (Rao et al., 1989); exclusive occupancy of the Al sixfold-coordinated interstitial site

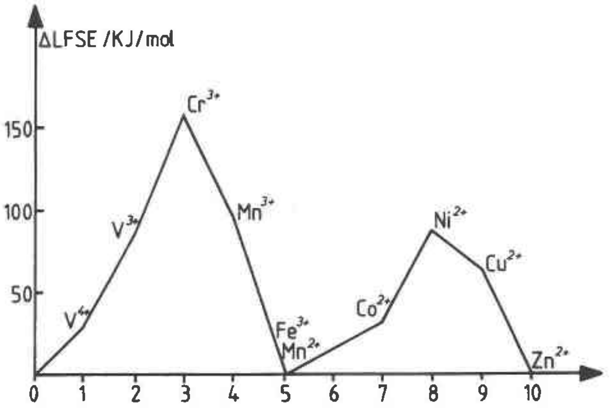

Fig. 1. Site preference energies for octahedral coordination of transition-metal $d^n$ ions with O as ligand.

could be explained in terms of kinetic factors relating to the coordination of $Mn^{2+}$ in the growth medium, even though the large difference in ionic radii of Al and Mn does not favor incorporation into the tetrahedral sites in quartz.

$Fe^{3+}$ is found in both tetrahedral and interstitial sites in quartz (Stegger and Lehmann, 1989). Although substitution in tetrahedral sites is always dominant in amethyst, synthetic crystals with exclusive occupancy of $Fe^{3+}$ in interstitial sites have been hydrothermally grown using seed crystals flattened on [001] with preferential growth along the **c** axis. Thus, seed orientation (or growth plane) seems to be an important kinetic factor. Although an overwhelming body of evidence in favor of occupancy of the interstitial sites has accumulated (Stegger and Lehmann, 1989), this relation is still disputed, and a substitutional center without local charge compensation has been proposed instead (Mombourquette and Weil, 1987; Mombourquette et al., 1989; Minge et al., 1989a, 1989b, 1990; Choi and Weil, 1970).

For $Fe^{3+}$ in berlinite, the same kind of interstitial incorporation was postulated on the basis of an SPM analysis (Heming and Lehmann, 1987) of its ZFS pattern, which implies an axis of compression along the threefold screw axis, like the interstitial center in quartz (Behner et al., 1986). The fourfold- and sixfold-coordinated sites in sillimanite were both indicated, as in the case of andalusite (Holuj and Jesmanowicz, 1978), to be occupied by $Fe^{3+}$ (Le Marshall et al., 1971).

## THE SIZE MISMATCH

For ions occupying sites of smaller host ions, the largest site is preferentially occupied, and thus the size mismatch is minimized. This principle appears to hold in numerous cases, e.g., for $Fe^{3+}$ and $Cr^{3+}$ in Al sites, as shown by SPM analyses (Newman and Urban, 1975) of ZFS data (Buscher et al., 1987).

$Cr^{3+}$ preferentially occupies (Barry and Troup, 1970; Troup et al., 1982) the larger M1 of the two sixfold-coordinated sites in chrysoberyl (Farbell et al., 1963), whereas in synthetic crystals grown from the melt, an intrasite partition coefficient higher than 3 (Forbes, 1983) was determined in favor of the same site. In zoisite, exclusive occupancy of the larger Al1 site by $Cr^{3+}$ (Hutton, 1971) is not surprising, in view of the large difference in average bond lengths of 0.08 Å (Dollase, 1968) between Al1 and Al2 sites.

Like $Cr^{3+}$, $Fe^{3+}$ shows preference for the larger sites in chrysoberyl and zoisite. However, exclusive occupancy of the slightly larger Al1 site ($\Delta R = 0.01$ Å) in cordierite (Gibbs, 1966) is indeed surprising (Hedgehock and Chakravarty, 1966). No site assignment was proposed initially by Hedgehock and Chakravarty (1966), since both Al sites have the same symmetry and thus cannot be distinguished by their site splittings, but the SPM analysis allows a precise assignment (Buscher et al., 1987). The single center of $Fe^{3+}$ detected in scolecite (Hutton and Scala, 1976) was assigned to the larger Al1 site using SPM analysis, although an even smaller difference in size than in the case of cordierite (only 0.003 Å) is reported for the two Al1, Al2 fourfold-coordinated sites (Falth and Hansen, 1979).

$Mn^{2+}$ almost exclusively occupies the larger M2 site (Fujino et al., 1981) in forsterite (Michoulier et al., 1969). In synthetic willemite an intrasite partition coefficient of 2 in favor of the larger Zn site was observed, irrespective of the temperature of crystal growth, which varied between 773 and 1793 K (Perkins and Sienko, 1967; Howling, 1969).

Exclusive occupancy of the Ca sites by $Gd^{3+}$ and $Eu^{2+}$ in minerals also possessing Mg or Al sites (Morris, 1975) is in accordance with this principle of minimization of size mismatch, which is valid for smaller host sites. The results for occupancy of smaller host sites are presented in Table 1.

Data for distribution of transition-metal ions among larger host sites are much scarcer. $Fe^{3+}$ preferentially occupies the larger M2 site in synthetic forsterite (Niebuhr, 1975). A difference in intrasite partition coefficients between two samples with different total Fe contents (0.2 and 0.0006 wt%), favors the first sample by a factor of about 50 and cannot represent equilibrium distributions. Exclusive occupancy of Mg sites by $Fe^{3+}$ in dolomite (Prissok and Lehmann, 1986) cannot be considered as proof of a site preference because this ion may have been formed by ionizing radiation after growth, as a result of the initial presence of $Fe^{2+}$. A single center of $Fe^{3+}$ was also detected and assigned to the Mg site in diopside (Gaite and Michoulier, 1973). Again, since no indication of local charge compensation was observed, it may also have been formed from $Fe^{2+}$ by exposure to ionizing radiation.

$Mn^{2+}$ in apatite prefers the Ca site, which is ninefold-coordinated by O, over the site coordinated by six O atoms and two monovalent ions (Warren, 1970). Because of their different coordination numbers and ligands, it is not easy to evaluate precisely the relative sizes of these sites.

**TABLE 1.** Site distributions for smaller host ions

| Mineral | Host site | c.n. | $\Delta R$* (Å) | $K$** $Fe^{3+}$ | $K$ $Cr^{3+}$ | $K$ $Mn^{2+}$ | References |
|---|---|---|---|---|---|---|---|
| Zoisite | Al1 | 6 | 0.78 | >20 | >20 | | Hutton (1971) |
| | Al2 | 6 | | | | | |
| Chrysoberyl | Al1 | 6 | 0.47 | >20 | 3.6 + 0.6 | | Barry and Troup (1970) |
| | Al2 | 6 | | | | | Forbes (1983) |
| Cordierite | Al1 | 4 | 0.10 | >20 | | | Hedgehock and Chakravarty (1966) |
| | Al2 | 4 | | | | | |
| Scolecite | Al1 | 4 | 0.03 | >20 | | | Hutton and Scala (1976) |
| | Al2 | 4 | | | | | |
| Tremolite | M1 | 6 | −0.02 | | | >9† | McGavin et al. (1982) |
| | M2 | 6 | 0.01 | | | >9 | |
| | M3 | 6 | | | | | |
| Forsterite | M1 | 6 | 0.38 | >2‡ | <1 | >20 | Niebuhr (1975), Rager (1977) |
| | M2 | 6 | | | | | Michoulier et al. (1969) |
| Willemite | M1 | 4 | 0.12 | | | 2 | Perkins and Sienko (1967) |
| | M2 | 4 | | | | | Howling (1969) |

* $\Delta R$ is the difference in average bond lengths.

** $K$ is the ratio of intrasite coefficients for the smaller over that of the larger site.

† The low occupancy ratio of Mg2 may be due to large differences in individual bond lengths of 1.2 Å. No distinction between Mg2 and Mg3 is possible from superposition model analysis.

‡ The distribution coefficients for two synthetic crystals differ by a factor of 50.

The slight preference of $Cr^{3+}$ for the smaller M1 site (Rager, 1977) in forsterite was explained by the larger ligand field stabilization energy for this site caused by the greater distortion.

## PREFERENCE OF $Mn^{2+}$ AMONG Mg AND Ca SITES

The ionic radius of $Mn^{2+}$ ranges between those of $Mg^{2+}$ and $Ca^{2+}$ (Shannon, 1976). With few exceptions, the Mg sites are preferentially occupied when both Ca and Mg sites are present (see Table 2).

The largest body of experimental data for structures with both Ca and Mg sites has been accumulated for dolomite, for which huge variations in the Mg/Ca distribution ratios were observed. If equilibrium distributions are established, the intrasite partition coefficient should approach unity at high temperatures. However, in one case (Angus et al., 1984), increases in intrasite partition coefficients with increasing temperature were reported, and the large value of 115 J/(mol·K) for the entropy difference calculated from them is not acceptable: it should be close to zero. The value of 9 J/(mol·K) calculated from results of another study (Lloyd et al., 1985) appears to be reasonable. In addition, the variation of a factor of about 200 among samples in a third study (Prissok and Lehmann, 1986) was shown to be too large to be compatible with equilibrium distributions. A second group of dolomite samples was found by Lloyd et al. (1985) to exhibit no correlation between intrasite partition coefficients and temperature.

For tremolite, three Mg sites (M1–M3) and one Ca site (M4) are available (Hawthorne and Grundy, 1976). Earlier studies (Bershov et al., 1966; Manoogian, 1968; Golding et al., 1972) had detected only a single center of $Mn^{2+}$, but additional weaker spectra were observed in a more recent investigation (McGavin et al., 1982); the most intense of those was assigned to the Ca site. However, this result is questionable, since the small size of the $^{55}Mn$ hyperfine splitting constant (isotropic value of $-74.8 \times 10^{-4}$ cm$^{-1}$) suggests occupancy of a Mg site (Simanek and Muller, 1970), whereas the value that is 15% higher than that reported for the less intense centers is in the range expected for Ca sites. As shown in Figure 2, occupancy of the M1, M3 (Mg), and M4 (Ca) sites is compatible with results of SPM analyses for the most intense center. Since M1 has a larger average bond distance than M3, it should be the one that is preferentially occupied, according to the principle of size mismatch. A possible cause for the low occupancy of the M2 site (despite its having even larger average bond distance than M1) may be the variation of the individual O bond lengths for this site, although they are not very large (0.09 and 0.02 Å for M3 and M2, respectively).

In monticellite, exclusive occupancy of the Mg site (Onken, 1965) by $Mn^{2+}$ was observed (Danilov and Manoogian, 1968).

For diopside, different intrasite partition coefficients have been reported, with some data showing preferential occupancy of the Mg site (Gaite, 1975) and other data implying nearly equal occupancy of Ca and Mg sites (Vinokurov et al., 1964). The results of an SPM analysis (Lehmann, 1982) and the sizes of the hyperfine splittings led to reversal of the site assignment proposed initially

**TABLE 2.** Distribution of $Mn^{2+}$ between Mg and Ca sites

| Mineral | $K$ = Mg/Ca | References |
|---|---|---|
| Dolomite | 2.7 ~ 500 | Angus et al. (1984) |
| | | Lloyd et al. (1985) |
| | | Prissok and Lehmann (1986) |
| Diopside* | <1** | Vinokurov et al. (1964) |
| | 7.5 | Gaite (1975) |
| Monticellite | >50 | Danilov and Manoogian (1968) |
| Tremolite* | >9 | McGavin et al. (1982) |

* Site assignments still controversial.

** The value of 1/$K$ slightly larger than 1.

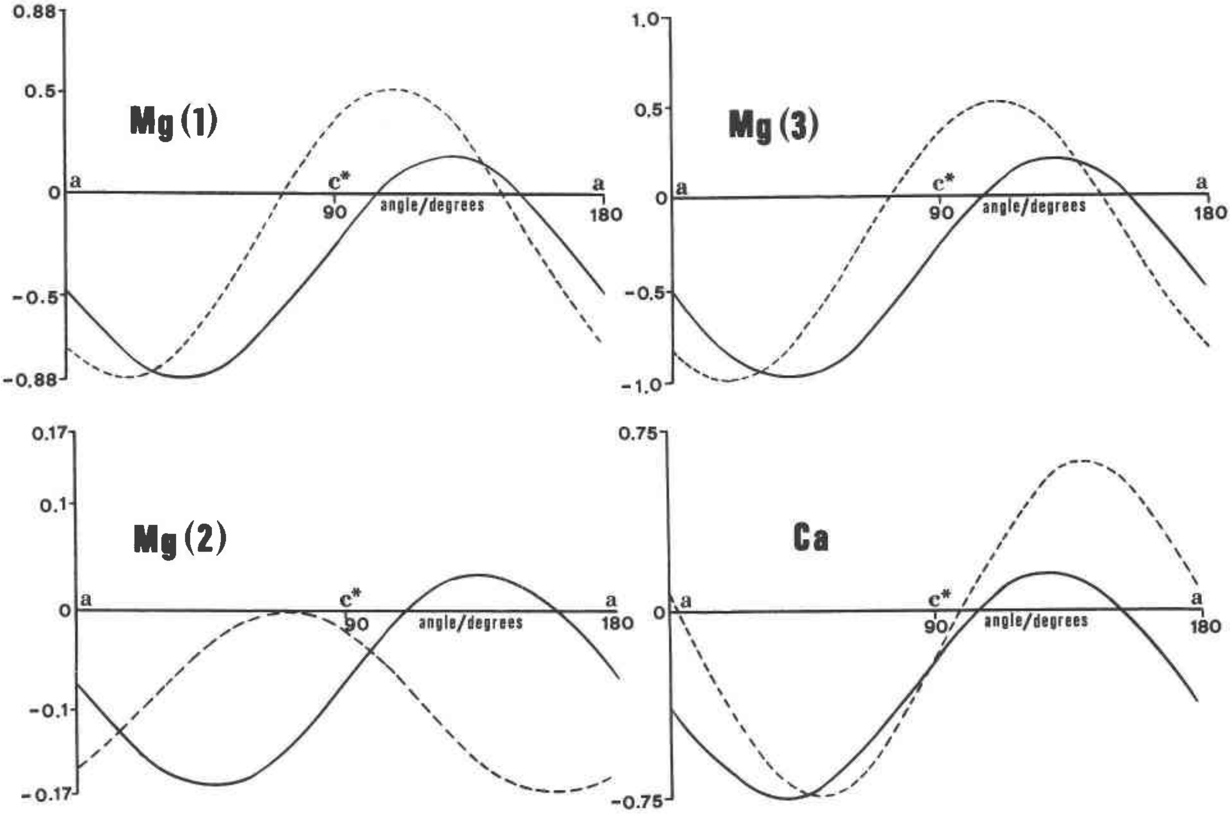

Fig. 2. Comparison of the zero field splitting pattern of the most intense spectrum of $Mn^{2+}$ in tremolite for rotation around the **b** axis (solid lines) with the distortion patterns of the four sites of divalent cations calculated from the crystal structure data (dashed lines). Both quantities are drawn as dimensionless distortions (=effective fractions of a ligand at normal bond distance; see Heming and Lehmann, 1987). Clearly the ZFS pattern is almost equally compatible with occupation of the Mg1, Mg3, and Ca sites.

for this mineral by Gaite (1975). Table 2 summarizes the results for distribution of $Mn^{2+}$ among Mg and Ca sites.

## Tendency of $V^{4+}$ for formation of a short V-O bond

This ion has a strong tendency to form a very short V-O bond, which results in one very large principal value of the $^{51}V$ hyperfine splitting constant, $A_{zz}$, the other two principal values $A_{yy}$, $A_{xx}$ are normally about three times smaller and of similar magnitude (see Table 3). $A_{zz}$ is approximately aligned along the V-O bond direction, which defines the O atom involved in the V-O bond. The observed inequality $g_{\parallel} < g_{\perp}$ is characteristic of a $VO^{2+}$ molecular ion because in a tetragonally compressed octahedron the $b_{2g}$ $(d_{xy})$ level is lowest.

In most cases it is advantageous to consider the coupled substitution of V and $O^{2+}$ in the host compound. So far, such coupled substitutions with perfect local charge compensation have been observed for three cations, Ti, Al, and Ca, in combination with different ligands, namely Ti-O and Al-OH or Al-F and Ca-$H_2O$.

$VO^{2+}$ was detected by EPR in titanite from different localities. Evidently, those samples all contain V in concentrations up to 0.3 mol% (Taborsky, 1976). In all cases, the spectra from a single center were observed (Bershov and Marfunin, 1965; Marfunin et al., 1966; Vassilikou-Dova and Lehmann, 1988a). As determined from the EPR data, the V-O bond is parallel to the Ti-O1 direction with a very short bond distance of 1.7 Å (Speer and Gibbs, 1976), as expected from the energetic preference for formation of a short V-O bond. The existence of a longer distance (by 0.2 Å) for the next shortest Ti-O bond explains why only one such center is observed. The presence of $V^{4+}$ in Si sites cannot, however, be excluded, since in such fourfold-coordination it can normally be detected only at or below 77 K (Grunin, 1971; Manoharan et al., 1968; Havlicek and Novak, 1974; De Biasi, 1980; Di Gregorio et al., 1982). The two EPR studies of Marfunin et al. (1966) and Vassilikou-Dova and Lehmann (1988a) were performed at room temperature.

In wavellite, two crystallographically nonequivalent Al sites each have two OH groups in their first coordination spheres (Araki and Zoltai, 1968). The EPR spectrum of a prominent center of $VO^{2+}$ with the **z** axis almost coincident with the **c** axis was obtained (Vassilikou-Dova et al., 1988), indicating substitution of axial symmetry, i.e., with local charge compensation. The direction of the V-O bond, as shown by the strongly absorbing center, clearly

**TABLE 3.** Spin-Hamiltonian parameters ($A$ in $10^{-4}$ cm$^{-1}$) and mode of substitution for $VO^{2+}$ in minerals

| Mineral | $g_\parallel$ $g_{zz}$ | $g_\perp^*$ $g_{yy}$, $g_{xx}$ | $A_\parallel$ $A_{zz}$ | $A_\perp^*$ $A_{yy}$, $A_{xx}$ | Host atoms | Site symmetry | References |
|---|---|---|---|---|---|---|---|
| Titanite | 1.943 | 1.958 | 174.3 | 54.8 | Ti-O1 | 1 | Marfunin et al. (1966)<br>Vassilikou-Dova and Lehmann (1988a) |
| Apophyllite | 1.933 | 1.974 | 180.2 | 60.6 | Ca-$H_2O$ | 1 | Marfunin et al. (1966) |
| | 1.948 | 1.96 | 166.2 | 59 | K-$H_2O$ | 1 | Vassilikou-Dova and Lehmann (1988b) |
| Wavellite | 1.932 | 1.948 | 171.8 | 54.7 | Al1-H1 | m | Vassilikou-Dova et al. (1988) |
| | 1.944 | | 151 | | Al1-O2 or | m | |
| | | | | | Al1-$H_2O$1 | 1 | |
| Zoisite | 1.948 | 1.955 | 163.4 | 51.2 | Al1-OH | 1 | Hutton (1971) |
| | 1.938 | 1.936 | 161.7 | 48.8 | Al3-O8 | m | |
| | 1.876 | 1.981 | 155.5 | 61.6 | | m** | |
| | 1.934 | 1.944 | 163.7 | 52.9 | Si3-O6 | m** | |
| Topaz | 1.946 | 1.974 1.998 | 148.1 109.8 | 43.4 | Al-F | 1 | Petrov (personal communication) |
| | 1.939 | 1.969 1.989 | 164.8 100.2 | 56.1 | Al-O3 | 1 | |
| Vanadinite | 1.903 | 1.987 1.968 | 175.9 106.8 | 66.8 | V-O1 | m | Vassilikou-Dova and Lehmann (1989) |

* Average of $g_{xx}$ and $g_{yy}$ or $A_{zz}$ and $A_{xx}$ values; they are usually alike.
** Visible at or below 77 K only.

indicates that substitution of Al1-OH1 by $VO^{2+}$ occurs. Not unexpectedly, this is the shortest of all the four Al-OH bonds, but it also involves the Al site with the smallest average bond length (1.8 Å compared with 1.9 Å for Al2). Thus, the principle of size mismatch seems to be of little significance in the formation of the molecular ion $VO^{2+}$, perhaps because of the considerable rearrangements of the coordinating ions in order to create a short V-O bond of approximately 1.6 Å in length. The spectra of two additional $VO^{2+}$ centers with absorbing peaks of much lower intensity (about 4% of that of the prominent absorption peaks) were also observed. These centers may be due to the substitution of $VO^{2+}$ for Al1-O2, corresponding to the shortest of all the Al-O or Al1-$H_2O$1 bonds. In both cases, coupled substitution of an Al-O-P group by V-O would occur. Local charge compensation would thus require coupled substitution.

In zoisite, only one Al-OH group is present (Dollase, 1968), but four centers of $VO^{2+}$ were detected (Hutton, 1971). The spectra of the center of higher intensity imply site symmetry $\bar{1}$. The **z** axis very nearly coincides with that of the Al1-OH bond direction, indicating the same substitution as in the prominent center in wavellite. The agreement in orientation is much better than with the Al1-O4 bond direction that was originally proposed by Hutton (1971), although the latter bond is the shortest of the Al1 site; thus, it cannot be excluded. However, in contrast to the substitution for the Al-OH group, an additional charge-compensating substitution would be required. The spectra of the second center observable at room temperature have site symmetry 2. The center was attributed by Hutton (1971) to substitution for Al3-O8, which has the shortest Al-O bond to Al3. This conclusion is therefore plausible, despite the lack of any indication of local charge compensation. Spectra of lower intensity from two additional centers could only be detected at 77 K, so they most likely arise from substitution for Si.

The presence of $VO^{2+}$ in topaz in two different sites was reported in two papers (Dickinson and Moore, 1967; Petrov, 1983); however, only in the latter were spin-Hamiltonian parameters and orientations of the principal axes reported, which allow assignment of peaks to a specific site. The orientation of the **z** axis of one center indicates coupled substitution of the shorter Al-F by $VO^{2+}$, which is analogous to the centers with the most intense peaks in wavellite and zoisite. The **z** axis of the second center of $VO^{2+}$ is close to the Al-O3 bond direction, again the shortest of all Al-O bonds (Ribbe and Gibbs, 1971). Thus, as in zoisite and wavellite, peaks from a center requiring additional charge compensation are also present. However, the reported values of $A_{xx}$ and $A_{yy}$ for these centers are unusually large compared with the ones reported for all other $VO^{2+}$ centers in minerals. Corrected values of the spin-Hamiltonian parameters of $VO^{2+}$ in topaz are reported in Table 3 (Petrov, personal communication).

For apophyllite, spectra with peaks arising from two $VO^{2+}$ centers were recorded (Marfunin et al., 1966; Vassilikou-Dova and Lehmann, 1988b). Substitution of Ca-$H_2O$ is undoubtedly responsible for the creation of the most prominent center, since in certain orientations a clear additional doublet hyperfine splitting due to interaction with a neighboring $F^-$ ion was observed (Ca is coordinated by four O atoms, two $H_2O$ molecules, and one F atom; Colville and Anderson, 1971). The less intense center was tentatively assigned to substitution of $K^+$ (coordinated by eight $H_2O$ molecules), since no additional ligand hyperfine splitting was observed, but substitution for Si also cannot be excluded. While substitution of M-$H_2O$ by V-$H_2O$ has been reported for numerous synthetic crystals (Jain and Venkateswarlu, 1980; Jain et al., 1984), apophyllite is the only known example of a mineral in which such substitution occurs.

The rule that the shortest bond is involved in the formation of the V-O molecular ion, verified in all the above cases, does not apply in a vanadinite sample from Turkey in which $V^{4+}$ was detected by EPR at room temperature (Vassilikou-Dova and Lehmann, 1989). The tetravalent ion evidently occupies a $V^{5+}$ site. The large distortion of this fourfold-coordinated site most likely causes an increase in the spin lattice relaxation time sufficient to be detected at room temperature. The direction of the z axis indicates that the V-O1 with the longer bond distance (1.76 Å) compared with the other two bonds (V-O3 = 1.72 Å) (Trotter and Barnes, 1958) corresponds to the short V-O bond. Since a shortening of more than 0.1 Å must take place after the formation of the double bond, differences in the dynamic properties of these bonds may be decisive. It is most likely that this ion forms as a result of low $f_{O_2}$ during crystal growth and not as a radiation defect.

## CONCLUSIONS

Existing data allow the formulation of qualitative rules for site preferences of transition-metal impurities: (1) the differences in ligand field stabilization energy for distribution among sites of sixfold- and fourfold-coordination controls substitutions by $Cr^{3+}$. However, the incorporation of $Mn^{2+}$ and $Fe^{3+}$ in interstitial sites of sixfold-coordination in minerals that normally have only fourfold-coordinated sites cannot be explained accordingly. (2) Where two or more sites of different size occur, occupancy of the larger site is preferred. (3) The choice of the shortest M-L bond (L = O, OH, F, or $H_2O$) for incorporation of a $VO^{2+}$ molecular ion has been verified in all cases, even if the principle of minimization of size mismatch is violated. The formation of a short V-O bond must be controlled by equilibria. Dynamic properties of bonds in addition to static differences must be of some influence. (4) A preference of $Mn^{2+}$ among Mg and Ca sites for the Mg site is normally observed. The large spread of distribution ratios in some systems, e.g., in dolomite, must be considered in connection with different geochemical environments and thermal histories. Contradictions among existing results show that other factors, such as initial Mg-Ca disorder at high temperatures or a different supply of $Ca^{2+}$ and $Mg^{2+}$ during crystal growth, must be considered.

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