

The effect of pressure on the degree of covalency of the cation–oxygen bond in minerals

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Abstract

The effect of pressure on the covalencies of Cr³⁺–, Fe³⁺–, and Fe²⁺–oxygen bonds in synthetic and natural garnets and pyroxenes has been investigated up to 200 kilobars. The results gained from this study indicate a slight decrease in Racah parameter, B, with pressure and consequently an increase in the degree of covalency of the cation–oxygen bond. The pressure-induced covalency increase is not expected to have appreciable influence on the ionicity of the M–O bond in upper mantle minerals, and the ionic model of the chemical bond is predicted to hold up through the transition zone. The magnitudes of energy changes in B with pressure have been correlated with shortened transition metal ion–ligand distances. With increasing pressure up to 200 kilobars, there appears to be a shortening in the average Cr³⁺–O bond distance by 0.7–1.0 percent and a decrease in B energy value by 1.5–2 percent; OH[–] ligands replacing oxygen anions around the central cation increase significantly the ionicity of the average M–O bond, and hence the average B energy value.

Introduction

There have been many speculations concerning the composition of the earth's mantle and the nature of the chemical bond in mineral phases occurring at great depths in the earth's interior (Anderson and Jordan, 1970; Gaffney, 1972; Huggins, 1975). In addition, it is not well known whether a covalent model for the M–O bonds in mantle minerals would be more appropriate than an ionic one.

It is generally accepted, however, that the covalency of the metal–ligand bond will increase with pressure due to the decrease in interatomic distances (Stephens and Drickamer, 1961; Shannon and Vincent, 1974; Abu-Eid, 1975a,b; Huggins, 1975).

The electronic repulsion, Racah parameter B has been used as an indicator of the degree of covalency of the chemical bond in natural and synthetic minerals (Manning, 1970; Moore and White, 1972; Abu-Eid, 1975a,b). Since the energies of many crystal field bands depend on the degree of covalency, a study of the pressure effect on absorption bands could reveal information on the nature and character of the bonds between transition metal ions and the

ligands in mineral phases existing under elevated pressure conditions in the mantle.

The present study is an attempt to use the high pressure electronic absorption spectroscopy technique for evaluation of the covalent character of the Cr³⁺–, Fe³⁺–, and Fe²⁺–oxygen bonds in minerals subjected to pressures up to 200 kbar.

The degree of covalency β

The degree of covalency of a metal–ligand bond in a complex may be determined using the covalency parameter², β , which is equivalent to the ratio of Racah parameter B in the complex to that of the free cation, B₀ (Tanabe and Sugano, 1954; Jorgensen, 1962; Griffith, 1964). The B energy value of a transition metal ion could be determined experimentally from spectral bands corresponding to electronic transitions whose energies are directly related to B.

It should be mentioned that β is related to two parameters: first, a central field covalency parameter which arises from screening the nuclear charge of the cation by the ligand and designated³ as β_{35} ; and sec-

² β is also known as the nephelauxetic ratio.

³ The repulsion parameters containing e_g or (γ_3) orbitals only are designated as β_{35} , and those with t_{2g} or (γ_6) are given as β_{65} , whereas integrals containing both e_g and t_{2g} orbitals are designated as β_{35} (Reinen, 1969).

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ond, a symmetry-restricted covalency parameter which arises due to delocalization of d -electrons onto the ligands and designated as β_{33} and β_{55} (Lever, 1968; Reinen, 1969; König, 1971). In this study, transitions dependent only on the central field covalency, β_{35} , will be taken into account since their repulsion parameters are influenced by all d -orbitals.

Electronic transitions and Racah parameters

To evaluate β for a transition metal ion, it is essential that its spectrum gives rise to absorption bands, the energies of which can be expressed in terms of B . Since each of the transition-metal ions with the electronic configurations $3d^1$ and $3d^9$ has only one electronic data are those of d^3 and d^8 configurations because crystal field parameter, $10Dq$, it is not possible then to determine the covalencies of such cations from their spectral data. On the other hand, the remaining transition-metal ions of the first series have several transitions which are related to both parameters, $10Dq$ and B . It is mandatory then to determine the energies of at least two transitions so that B values may be evaluated.

For this study, the most appropriate transition metal ions that give directly B values from their spectral data are those of d^3 and d^8 configuration, because such cations each have one spin-allowed transition, the energy of which is equivalent to $10Dq$ and another whose energy is dependent on both $10Dq$ and B parameters. In addition, the B value for the second transition is related only to one type of covalency parameter, *viz.*, the central field covalency parameter β_{35} , *i.e.* it is not restricted to one type of orbital.

Let us now consider Cr^{3+} as an example of a d^3 cation. In an octahedral site, it has the following spin-allowed transitions

$${}^4A_{2g} \rightarrow {}^4T_{2g}(F) \text{ and designated as } \nu_1,$$

$${}^4A_{2g} \rightarrow {}^4T_{1g}(F) \text{ and designated as } \nu_2,$$

$$\text{and } {}^4A_{2g} \rightarrow {}^4T_{1g}(P) \text{ and designated as } \nu_3.$$

Since the B value of the ν_3 transition is also dependent on the symmetry restricted covalency parameter β_{35} , it will not be taken into account for the reason mentioned above. The energy value of ν_1 is equivalent to $10Dq$, and that of ν_2 is given as:

$$\nu_2 = 15Dq + 7.5B - 6B(1 + \mu)^{1/2} \quad (1)$$

where $\mu = [(10Dq - 9B)/12B]^2$. Equation (1) was derived from Tanabe and Sugano's (1954) matrix; the B value is then determined from the energies of the ν_1 and ν_2 transitions by means of the relationship:

$$B = 1/3[(2\nu_1 - \nu_2)(\nu_2 - \nu_1)/(9\nu_1 - 5\nu_2)] \quad (2)$$

Considering d^5 cations, *e.g.* Fe^{3+} and Mn^{2+} , B values may be estimated from the two spin-forbidden transitions: ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_g(G)$, and ${}^6A_{1g} \rightarrow {}^4E_g(D)$; those are designated here as ϵ_1 and ϵ_2 , respectively. The energy value of ϵ_1 is equivalent to $10B + 5C$, and that of ϵ_2 is $17B + 5C$ (Tanabe and Sugano, 1954). B will be equivalent then to $(\epsilon_2 - \epsilon_1)/7$. The above two transitions, ϵ_1 and ϵ_2 , usually give rise to conspicuous and sharp peaks in the spectra of natural minerals containing Fe^{3+} and Mn^{2+} cations (Manning, 1970).

In the case of the d^6 cation-type, *e.g.* Fe^{2+} and Co^{3+} , there is only one spin-allowed transition, *viz.*: ${}^5T_{2g} \rightarrow {}^5E_g$, whose energy is equivalent to $10Dq$. In addition, there are several spin-forbidden transitions dependent in their energies on B , C , and $10Dq$ parameters. For example, the energy of the transition ${}^5T_{2g} \rightarrow {}^1A_{1g}$ is equivalent to: $-20Dq + 5B + 8C - 120B^2/10Dq$ (Lever, 1968). Assuming that $C \cong 4B$ (Griffith, 1964), B may then be estimated from the above spin-forbidden transition, since $10Dq$ is obtained directly from the transition, ${}^5T_{2g} \rightarrow {}^5E_g$.

Experiments

The spectra of Cr^{3+} , Fe^{2+} , and Fe^{3+} cations contained in various minerals were studied under different pressures. The spectra were measured using the Cary 17 recording spectrophotometer with a newly constructed optical attachment that enables measurement to be made of the spectra of small crystal fragments (diameter $> 50\mu$) and of micro-powdered specimens subjected simultaneously to pressures of up to 200 kbar. The attachment is similar to that described by Bell and Mao (1972); Figure 1 illustrates the attachment components and the light path from the beam divider up to the detector.

The pressure instruments used in this study are the diamond pressure cells described by Bassett *et al.* (1967), and Abu-Eid (1975b). The pressure was calibrated using NaCl powder, mixed with the mineral sample in a 1:2 ratio, as an internal standard. A lead-glass collimator was attached to the diamond cell to collimate the X-ray beam to about 100μ . Although the collimation of X-rays increases significantly the exposure time, it reduces to a large extent the sample region whose pressure gradient is maximum.

Interference from the diamond absorption in the visible region was a major difficulty encountered in this study. The diamond absorption bands at wavelengths 415, 403, 394, and 384 nm overlap the spin-forbidden bands of Mn^{2+} , Fe^{2+} , and Fe^{3+} cations.

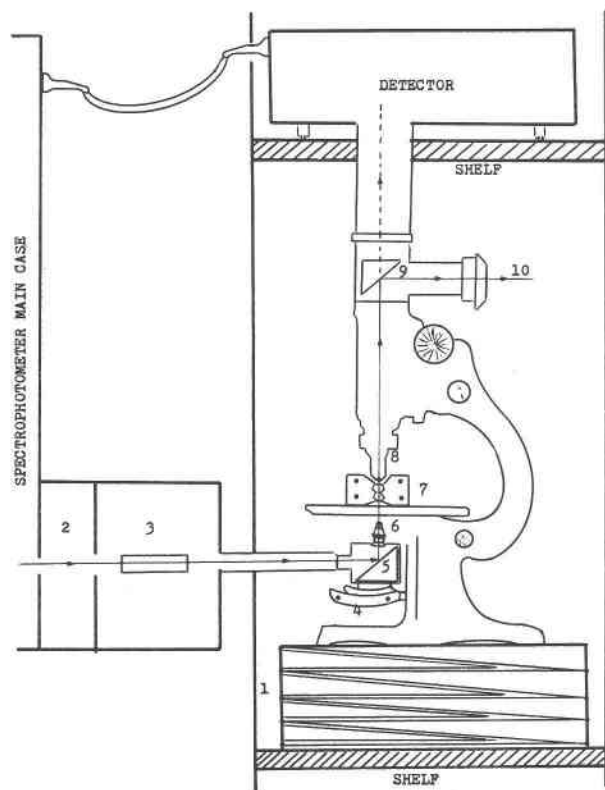


FIG. 1. The spectrophotometer optical attachment designed to enable the measurements of the spectra of microsamples ($\geq 50\mu$): 1. Jack, 2. Beam divider, 3. Polarizer, 4. X-Y mini-transfer stage, 5. Aluminum mirror, 6. Focusing lens (UMK50), 7. Diamond cell, 8. UMK50 objective lens, 9. Mirror-shutter combination, 10. Lateral eyepiece.

The absorption caused by the diamond anvils was reduced by mounting another diamond cell containing no sample in the reference beam.

Results

Spectral measurements were made on Cr^{3+} ions contained in uvarovite garnet, $\text{Ca}_3\text{Cr}_2^{3+}\text{Si}_3\text{O}_{12}$, which was synthesized by Huggins (1974) from a mixture of CaO , SiO_2 silica glass, and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ held for 5 days at 1 kbar and 675°C .

The spectra of the powdered garnet specimen mixed with NaCl were measured at five different pressures. Figure 2 shows the spectra recorded at 1 atm, 95 kbar, and 177 kbar. The two bands in the 1 atm spectrum at energies 15667 cm^{-1} and 22727 cm^{-1} are assigned to the electronic transitions ν_1 and ν_2 of Cr^{3+} . Using equation (2), the B energy values were calculated. B was also calculated using the B_0 energy-value, 918 cm^{-1} , reported by Griffith (1964). Those results are summarized in Table 1. It is evident from

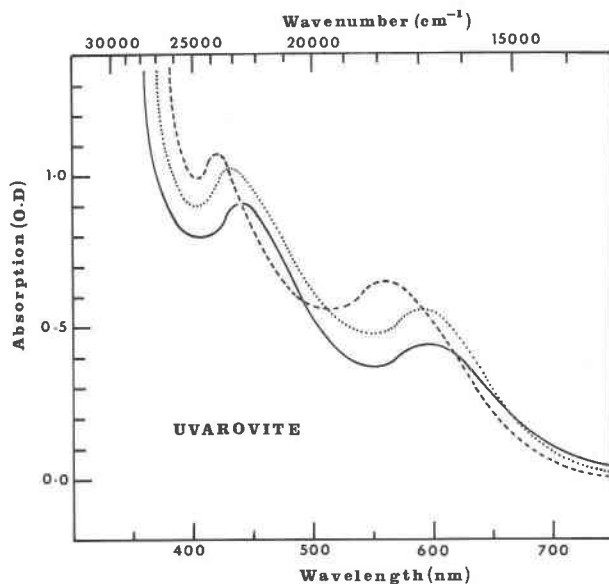


FIG. 2. The absorption spectra of synthetic uvarovite measured at 1 atm (—); 95 kbar (....); and 177 kbar (----).

Table 1 that there is a consistent slight decrease in the value of B with increasing pressure (about $0.067\text{ cm}^{-1}/\text{kbar}$).

The spectra of Fe^{2+} contained in orthoferrosilite, lunar pyroxene, and olivine (fayalite) were measured at various pressures. In all of these measurements, intense absorption bands corresponding to the spin-allowed transition of Fe^{2+} were observed in the near i.r. region. In addition, many weak, but conspicuous, peaks were observed in the visible region at energies around 18180 , 19850 , and 22990 cm^{-1} . Such peaks were assigned to the spin-forbidden transitions in Fe^{2+} (Burns *et al.*, 1972). The γ -spectrum of an orthoferrosilite single crystal recorded at 1 atm and 20 kbar is shown in Figure 3. At elevated pressures, there is a consistent shift of the bands in the i.r. region to higher energies, indicating that there is an increase in $10Dq$ parameter with pressure. The high pressure spectra of orthoferrosilite in the near i.r.

TABLE 1. The energy values of the electronic transitions ν_1 and ν_2 of Cr^{3+} in uvarovite measured at five different pressures*

Pressure	$\nu_1\text{ (cm}^{-1}\text{)}$	$\nu_2\text{ (cm}^{-1}\text{)}$	$B\text{ (cm}^{-1}\text{)}$	β
1 atm	16667	22727	589	0.6416
42 kb	16810	22846	585	0.6372
95 kb	17007	23041	582	0.6340
177 kb	17668	23697	577	0.6285
197 kb	17820	23840	575	0.6236

*The B energy value at each pressure was computed using equation (2), and β was calculated using the B_0 energy value (918 cm^{-1}) reported by Griffith (1964).

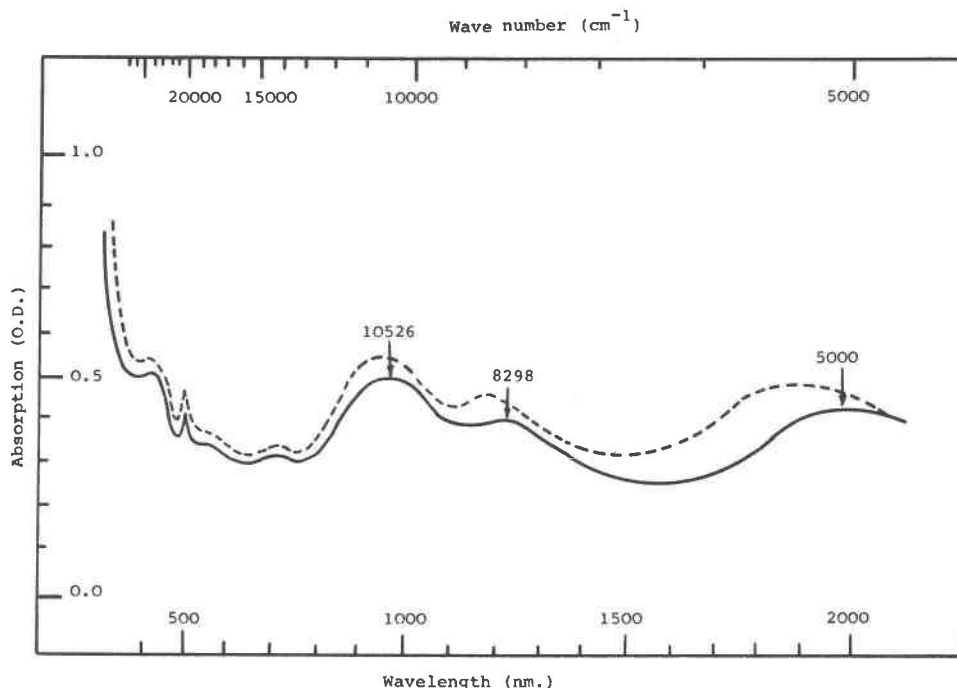


FIG. 3. The γ -spectrum of orthoferrosilite ($\text{Fs}_{86}\text{En}_{14}$) recorded at 1 atm (—) and 20 kbar (-----).

region (2100–800 nm) were also reported by Mao and Bell (1970). The results of Mao and Bell are, in general, consistent with those obtained from this study.

On the other hand, the less intense absorption peaks in the visible region, which were assigned to the spin-forbidden transitions in Fe^{2+} , did not show any significant shift. Since the spin-forbidden transitions are dependent mostly on B and C, and to a lesser extent on $10Dq$, it is concluded that the negligible energy shift of these bands is further evidence demonstrating the slight change in Racah parameters at elevated pressures.

Parallel results were obtained for Fe^{3+} -bearing garnets which usually show two sharp peaks at energies around 22600 and 24000 cm^{-1} . These are related to the transitions ϵ_1 and ϵ_2 explained above. Absorption peaks related to these transitions were also observed in the spectra of andradite, omphacite, epidote, and glaucophane. With increasing pressure up to 50 kbar, no measurable energy shifts of Fe^{3+} peaks were observed, indicating the negligible energy change of B and C parameters with pressure.

Discussion

It was mentioned earlier that the interelectronic repulsion integrals, which are expressed in terms of Racah parameters B and C, are directly related to the

degree of covalency of the metal-ligand bond in the complex. In addition, they are proportional to the average reciprocal radius, $\langle r^{-1} \rangle 3d$, of the partly filled 3d shell.

Considering Cr^{3+} -complexes, the B value of Cr^{3+} depends also on other factors such as the nature of the ligands surrounding the cation, the M-L interatomic distances, and the relative concentration of Cr^{3+} ions in the complex (Reinen, 1969; Poole and Itzel, 1963; Poole, 1964).

Reinen (1969) reported that Δ_o^4 and B values for $\text{Cr}_x\text{Al}_{2-x}\text{O}_3$ mixed crystal series vary with the concentration of Cr^{3+} ions. Reinen found that both Δ_o and B values decrease with increasing x. The decrease in Δ_o is easily explained because the Cr^{3+} site expands with increasing x. However, the decrease in B may be due to an increase in the degree of delocalization of d-electrons onto the ligands as the chromium content increases. This is reflected in the higher electro-negativity of Cr^{3+} relative to Al^{3+} .

The B value is expected to decrease with decreasing M-L interatomic distance due to the increase in the degree of metal-ligand orbital overlap which then causes an increase in the radius of the partly filled 3d shell.

⁴ Δ_o is equivalent to $10Dq$.

In this study, therefore, the degree of covalency was examined in various minerals and correlated with the average Cr–O distances. Burns (1975) has listed the energies of ν_1 and ν_2 transitions in Cr^{3+} ions contained in a suite of natural minerals. Burns also listed the average M–O distances in these minerals and CFS^b and CFSE^c parameters. From the energy values of ν_1 and ν_2 transitions, B values have been calculated for Cr^{3+} ions in those minerals. Figure 4 shows the trend of B values with changes in Cr–O distances. From Figure 4 it is apparent that there is a slight decrease in B value as M–O distance decreases. However, some minerals (epidote, tremolite, and tourmaline) fall far away from this trend. These min-

erals have substantially larger B values compared to the remaining minerals. After surveying the nature of ligands surrounding the Cr^{3+} ions in these minerals, we notice that the Cr^{3+} ion is surrounded by 4 oxygens and two OH^- ions, whereas in other minerals it is surrounded by 6 oxygens. The large B value in the hydroxyl-bearing minerals appears to be related to replacing two oxygens by two OH^- ions. Since the OH^- ion has one negative charge less than O^{2-} , it is expected to have a smaller electron density than O^{2-} to overlap onto the Cr^{3+} d -orbitals. Consequently, when the Cr^{3+} cation is coordinated to OH^- ions, the radius of the partly filled $3d$ shell is expected to be smaller than the case when Cr^{3+} is coordinated only to oxygens; thus, B values should be larger for hydroxyl-bearing minerals.

It is also observed in Figure 4 that Cr^{3+} in eskolaite (Cr_2O_3) has a very low B value. This is in fact expected since the chromium content is very large (Reinen, 1969).

^b CFS is the crystal-field splitting parameter which is equivalent to $10Dq$ in an octahedral site.

^c CFSE is the crystal-field stabilization energy of the transition-metal ion.

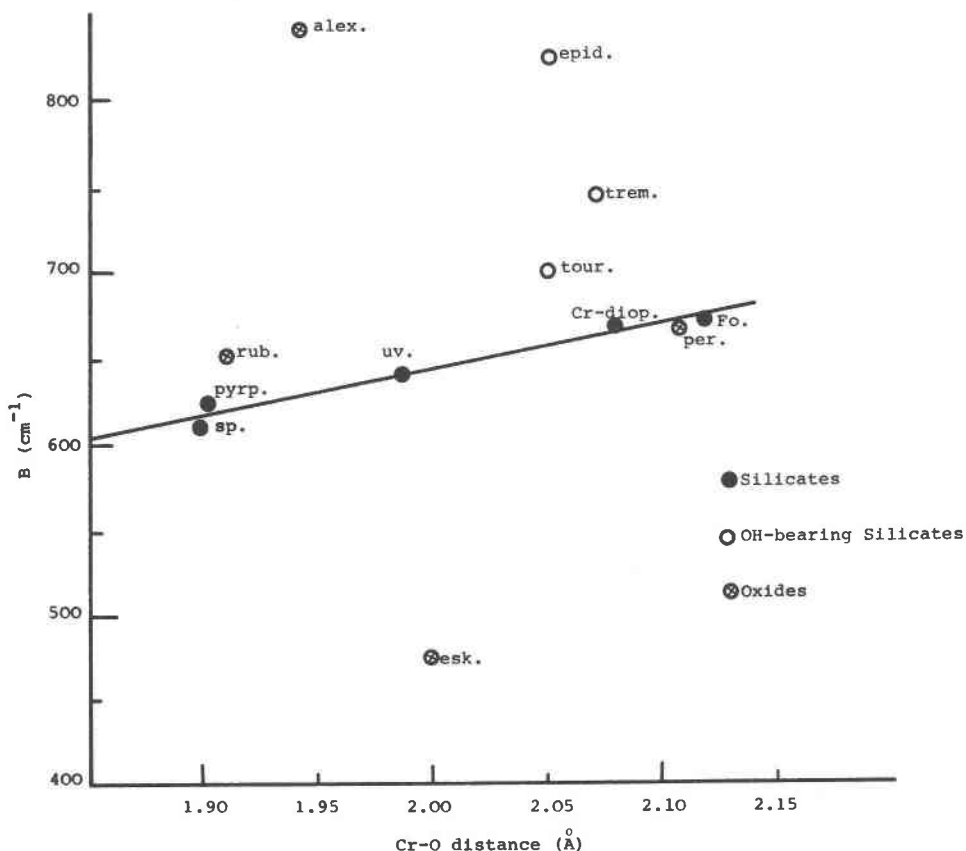


FIG. 4. The variation of B value with Cr–O distance in a suite of chromium minerals. The B value for each mineral was computed using the energies of ν_1 and ν_2 transitions tabulated by Burns (1975) and the relationship given in (2). Mineral names are abbreviated as follows: epid: epidote; alex: alexandrite; trem: tremolite; tour: tourmaline; Cr-diop: Cr-diopside; Fo: forsterite; per: periclase; uv: uvarovite; rub: ruby; pyrp: pyrope; sp: spinel; and esk: eskolaite.

With increasing pressure, the M-L interatomic distances will decrease; consequently, a decrease in B value should be expected.

The slope of the line shown in Figure 4 indicates that the rate of change of B with shortening Cr-O distance is about $50 \text{ cm}^{-1}/0.1 \text{ \AA}$. The change in Cr-O distance at elevated pressure may be roughly estimated from $10Dq$ values obtained at these pressures.

From the energy values of Δ_p ($10Dq$ at high pressure) and Δ_o ($10Dq$ at 1 atm) for Cr^{3+} , which are listed in Table 1, and considering the equivalence from the point charge model:

$$\Delta \equiv 10Dq \propto 1/R^6 \quad (3)$$

where R is the M-L distance, the following relationship was derived:

$$[\Delta_o/\Delta_p] = [(Cr-O)_p/(Cr-O)_o]^6 \quad (4)$$

Considering the average Cr-O distance in uvarovite at normal pressure as 1.986 \AA ; Δ_o 16667 cm^{-1} ; $\Delta_{95 \text{ kbar}}$ 17007 ; and $\Delta_{177 \text{ kbar}}$ 17668 cm^{-1} , then the average Cr-O distance decreases by about 0.010 and 0.014 \AA respectively at these pressures. Considering this decrease and the slope of the line shown in Figure 4, it appears that the value B will decrease at 95 and 177 kbar by 5 cm^{-1} and 10 cm^{-1} , respectively. These changes in B value are in good agreement with those obtained experimentally, namely 7 cm^{-1} and 12 cm^{-1} . It should be mentioned that Minomura and Drickamer (1961) and Stephens and Drickamer (1961) reported a pressure-induced energy decrease in the energy value of B of Cr^{3+} ions doped in MgO and Al_2O_3 . They obtained a decrease in B value of 20 cm^{-1} with increasing pressure up to 140 kbar. Thus their results agree, in general, with those reported in this study. However, the larger energy decrease obtained by the above authors may be due to the fact that doped cations usually occupy larger sites than the host cations. Hence, such cations may have different cation-ligand distances and possibly more ionic behavior. The experimental results obtained in this study and the argument presented above show that the B value decreases very slightly with increasing pressure and with decreasing M-O distances.

A further indication of the slight decrease in B value stems from the high-pressure studies of the spectra of Fe^{3+} and Fe^{2+} ions in silicate minerals. As it was mentioned earlier, no detectable energy shifts have been observed at elevated pressures in spectral bands corresponding to the spin-forbidden transitions in these cations. However, these shifts were estimated from the high-pressure spectra not to exceed

100 cm^{-1} in 50 kbar. Assuming that C is approximately equivalent to 4B (Griffith, 1964), then the energy of these transitions will be equivalent to 30B. Consequently, the change in B value in 50 kbar should be about 3.3 cm^{-1} . This change in B value is also consistent with the above argument and the results obtained for Cr^{3+} in uvarovite.

Conclusions

From the above discussion, it is apparent that changes in the degree of covalency of the Cr-O, Fe^{3+} -O, and Fe^{2+} -O bonds with increasing pressure up to 200 kbar are very small. This implies that the ionic model for the M-O bond in silicates still holds in the earth's mantle. It is expected, then, that changes in the structure, such as phase transitions or disproportionation to oxide components, may take place before any significant changes in the ionic character of the M-O bond occur.

It should be mentioned that the nature of the chemical bond in the oxides assumed to occur in the lower mantle is most likely to be of metallic character. The increase in the electrical conductivities of $(\text{Mg,Fe})_2\text{SiO}_4$ polymorphs at pressure above 100 kbar (Mao, 1973) and the shifts of their absorption edges to lower energies may be related to an increase in the metallic character of these phases. Such changes may be an intermediate stage that takes place before disproportionation of $(\text{Mg,Fe})_2\text{SiO}_4$ phases to their oxide components.

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