

Short-range order and long-range order in amphiboles: A model for the interpretation of infrared spectra in the principal OH-stretching region

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Abstract—The factors affecting the relative intensities of the four fine-structure bands in the principal OH-stretching region of the infrared spectrum of binary amphibole solid-solutions of the type ${}^cM^{2+}$ [$M=(Mg, Fe^{2+}), (Mg, Co^{2+})$] are examined. The band intensities are affected by both LRO (Long-Range Order) and SRO (Short-Range Order). If the LRO is characterized by a different method, (e.g., Rietveld structure refinement, single-crystal structure refinement), the expected band intensities can be calculated for this state of LRO; any deviation from the observed band intensities (corrected for variation in transition moment with absorption frequency) is due to SRO. The possible variations in band intensities are derived as a function of the different possible types of SRO, subject to the constraint that the state of LRO is fixed for a specific crystal. There are 22 different types of SRO that give rise to 16 different ways in which the observed band intensities can depart from the band intensities calculated for no SRO and a known state of LRO. In principle, SRO can be detected in this fashion provided the observed band-intensities can be corrected for variation in integrated molar absorptivity (transition moment) as a function of band energy.

INTRODUCTION

IN AMPHIBOLES, the fundamental band of the OH-stretching vibration in the infrared occurs in the range 3750–3600 cm^{-1} . Ordered end-member amphiboles have a single sharp band in this region. However, in intermediate-composition amphiboles, this band shows considerable fine-structure that may be attributed primarily to cation substitution effects at those cation sites coordinated by the hydroxyl ion. This fine-structure was first used by STRENS (1966) and BURNS and STRENS (1966) to characterize cation order over the M(1,2,3) sites in amphiboles, and extensive work on amphiboles was published in the following five years (see HAWTHORNE, 1981, 1983). However, several problems with the method gradually became apparent:

(1) The spectra are sensitive to all substituents at the M(1) and M(3) sites, and in chemically complicated amphiboles, the spectra can be too complicated to be adequately resolved.

(2) Substitution at cation and anion sites not coordinated directly to OH may broaden bands or even introduce new bands.

(3) Infrared spectroscopy is sensitive to both long-range order and short-range order, and it is still not clear whether or not these effects can be adequately distinguished by this method.

As a result of these problems, the method was little used in site-occupancy studies of amphiboles for ~15 years. However, the last six years have seen a revival of the method, specifically to charac-

terize ordering in synthetic amphiboles. In such work, problems (1) and (2) are not relevant because the composition of the amphibole is controlled as part of the experiment, and the spectral effects of specific components can be examined one at a time. This approach is the underlying methodology of the work by DELLA VENTURA and ROBERT (e.g., DELLA VENTURA, 1992; DELLA VENTURA and ROBERT, 1990; DELLA VENTURA *et al.*, 1991, 1993a, b; ROBERT *et al.*, 1989). However, because of problem (3), the infrared method has only been used in a qualitative fashion in this work (see also RAUDSEPP *et al.*, 1987a,b, 1991). In this paper, we consider the spectral effects of long-range order and short-range order on the infrared spectra of amphiboles in the principal OH-stretching region, and use some results from well-characterized synthetic amphiboles to test our model.

SHORT-RANGE ORDER (SRO) AND LONG-RANGE ORDER (LRO)

Previous investigators have used the terms 'segregation' and 'clustering' to designate various aspects of ordering in amphiboles that pertain to infrared spectroscopy. Both of these terms are superfluous. 'Segregation' is equivalent to long-range order (LRO) and 'clustering' is equivalent to short-range order (SRO); consequently, we will use the latter terms when referring to ordering in general. However, the terms 'clustering' and 'anti-clustering' are very useful to describe short-range arrangements with pair-correlations respectively

greater and less than that expected for no SRO, and hence we will use these terms here.

THE O(3) SITE

The O(3) site and its local environment is illustrated in Fig. 1; it can be occupied by OH⁻, F⁻, Cl⁻ (OBERTI *et al.*, 1993) and O²⁻ (HAWTHORNE *et al.*, 1995). When O(3) = OH⁻, the O(3)-H distance is ~0.96 Å (HAWTHORNE and GRUNDY, 1976) and the O-H bond is approximately orthogonal to (100) (HANISCH, 1966). The O(3) anion bonds directly to two M(1) and one M(3) cations (Fig. 1); although the point symmetry of the O(3) site is *m*, it is also pseudo-trigonal, a very important factor that affects the resolution of the infrared spectra (STRENS, 1966).

PREVIOUS WORK

Most work has focused on the situation where there are two cation species (*e.g.*, Mg, Fe²⁺) distributed over the M(1) and M(3) sites. As O(3) bonds to these M sites, there are 2 × 2 × 2 = 8 different possibilities for the local environment of an OH⁻ anion at the O(3) site (Table 1); however, the corresponding spectra show only four bands (*e.g.*, Fig. 2). This is a result of the pseudo-trigonal nature of the local arrangement; the M(1) and M(3) cations are pseudo-symmetrically related, introducing an accidental degeneracy into the spectrum (Table 1). In spectra such as that shown in Fig. 2, the peaks are labelled A, B, C and D, and the assignments are shown in Table 1.

STRENS (1966, 1974) derived criteria for identifying both LRO and SRO, but LAW (1976) showed that these were not correct. LAW (1976) developed

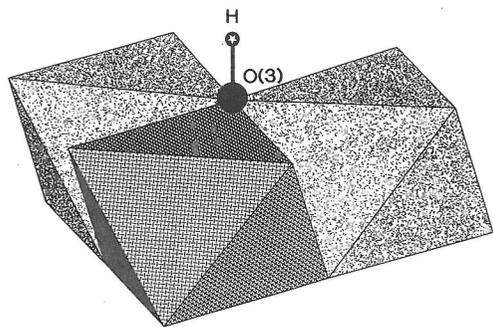


FIG. 1. The (OH) group in the amphibole structure, associated with the M(1) and M(3) coordination polyhedra. The M(1) octahedra are stippled, the M(3) octahedron is hatched, the oxygen atom at the O(3) site is shown as a black circle, and the H atom is shown as a starred circle.

Table 1. Possible local arrangements around the O(3) site in amphiboles with (Mg, M²⁺) at M(1) and M(3)

	M(1)	M(1)	M(3)	Band*	Band ⁺
(1)	Mg	Mg	Mg	A	A
(2)	Mg	Mg	M ²⁺	B'	
(3)	M ²⁺	Mg	Mg	B''	B
(4)	Mg	M ²⁺	Mg	B''	
(5)	M ²⁺	M ²⁺	Mg	C'	
(6)	M ²⁺	Mg	M ²⁺	C''	C
(7)	Mg	M ²⁺	M ²⁺	C''	
(8)	M ²⁺	M ²⁺	M ²⁺	D	D

* ideal band-structure; (3) and (4) are symmetry equivalent and give rise to only one band: B''; similarly (5) and (6) are symmetry equivalent and give rise to only one band: C''.

⁺ band structure usually observed; (2) and [(3)+(4)] are pseudo-symmetrically degenerate, and only one band (B) is observed experimentally; similarly, (5) and [(6)+(7)] are pseudo-symmetrically degenerate and only one band (C) is observed experimentally.

a model for LRO assuming that no SRO is present, but application to two amphiboles characterized by other means (Mössbauer spectroscopy, crystal-structure refinement) showed poor agreement between the various sets of results. WHITTAKER (1979) explored the spectral effects of possible models of SRO in amphiboles, and his results gave the impression that the resolution of SRO and LRO in amphiboles by infrared spectroscopy is not feasible.

THE CURRENT MODEL

We will consider binary occupancy of M(1) and M(3) by Mg and a transition metal M²⁺. Site occupancies and C-group compositions are denoted in the following way:

$$y_{M(1)} = M^{2+} \text{ at } M(1)$$

$$y_{M(3)} = M^{2+} \text{ at } M(3)$$

$$x_{M(1)} = \text{Mg at } M(1)$$

$$x_{M(3)} = \text{Mg at } M(3)$$

$$X = \text{total Mg at } M(1,3) = 2x_{M(1)} + x_{M(3)}$$

$$Y = \text{total } M^{2+} \text{ at } M(1,3) = 2y_{M(1)} + y_{M(3)}$$

(1)

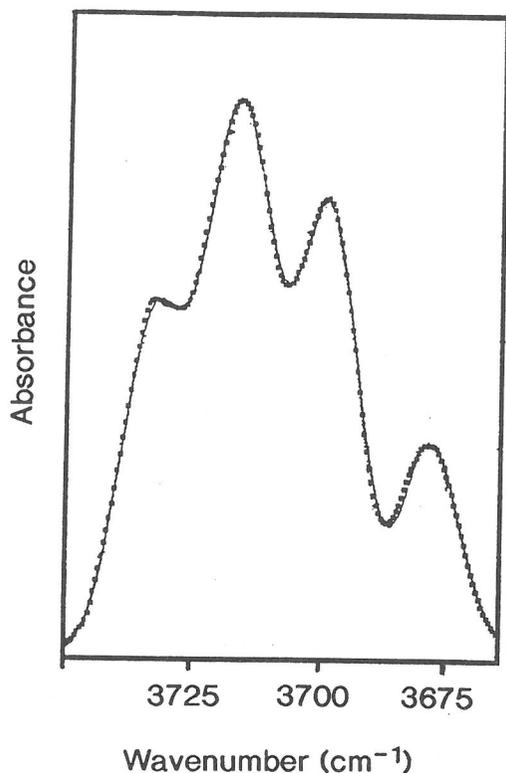


FIG. 2. The infrared spectrum in the principal OH-stretching region of a synthetic (Mg,Co)-potassium-rich-terite of composition $K(\text{CaNa})(\text{Mg}_3\text{Co}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$.

We can express *all* occupancies in terms of x and y by manipulating the individual terms of equation set (1):

$$\begin{aligned} x_{M(1)} &= 1 - y_{M(1)} = 1 - \frac{1}{2}[Y - y_{M(3)}] \\ y_{M(1)} &= \frac{1}{2}[Y - y_{M(3)}] \\ x_{M(3)} &= 1 - y_{M(3)} \end{aligned} \quad (2)$$

The case of no SRO

Following STRENS (1966, 1974) and LAW (1976), the (degenerate) relative band intensities, $I_{A,B,C,D}^C$, are given by

$$\begin{aligned} I_A^C &= x_{M(1)}^2 x_{M(3)} \\ I_B^C &= x_{M(1)}^2 y_{M(3)} + 2x_{M(1)} y_{M(1)} x_{M(3)} \\ I_C^C &= y_{M(1)}^2 x_{M(3)} + 2x_{M(1)} y_{M(1)} y_{M(3)} \\ I_D^C &= y_{M(1)}^2 y_{M(3)} \end{aligned} \quad (3)$$

where the superscript C on the band intensities

denotes that they are *calculated* values. Substituting (2) into (3) gives

$$\begin{aligned} I_A^C &= (1 - \frac{1}{2}[Y - y_{M(3)}])^2 (1 - y_{M(3)}) \\ I_B^C &= (1 - \frac{1}{2}[Y - y_{M(3)}])^2 \times y_{M(3)} \\ &+ 2(1 - \frac{1}{2}[Y - y_{M(3)}]) \times \frac{1}{2}[Y - y_{M(3)}] (1 - y_{M(3)}) \\ I_C^C &= \frac{1}{4}[Y - y_{M(3)}]^2 (1 - y_{M(3)}) \\ &+ 2(1 - \frac{1}{2}[Y - y_{M(3)}]) \times \frac{1}{2}[Y - y_{M(3)}] \times y_{M(3)} \\ I_D^C &= \frac{1}{4}[Y - y_{M(3)}]^2 \times y_{M(3)} \end{aligned} \quad (4)$$

These equations (set 4) give the calculated band intensities as a function of cation ordering (*i.e.*, $y_{M(3)}$) for a specific composition Y when there is no SRO present. Following LAW (1976), we may assume that there is no SRO and use equation (4) to derive the state of LRO in the amphibole from the *observed* values of the band intensities ($I_A^A, I_B^B, I_C^C, I_D^D$). Alternatively, we may measure the LRO (*i.e.*, $y_{M(3)}$) by some other method (*e.g.*, Rietveld structure refinement: RAUDESEPP *et al.*, 1987a,b; DELLA VENTURA *et al.*, 1993a,b) and use

Table 2. Behavior of band intensities* with short-range order

MgMgMg		$M^{2+}M^{2+}M^{2+}$	I_A^O	I_B^O	I_C^O	I_D^O
c^A	>	$2c^D$	U	D	u	u
c^A	=	$2c^D$	U	D	E	u
c^A	<	$2c^D$	u	D	d	u
c^A	>	c^D				
c^A	=	c^D	U	D	D	U
$2c^A$	>	c^D	u	d	D	u
c^A	<	c^D				
$2c^A$	=	c^D	u	E	D	u
$2c^A$	<	c^D	u	u	D	U
c^A		n^D	U	D	u	E
n^A		c^D	E	u	D	u
a^A	>	$2a^D$	D	U	d	d
a^A	=	$2a^D$	d	U	E	d
a^A	<	$2a^D$	d	U	u	d
a^A	>	a^D				
a^A	=	a^D	D	U	U	D
$2a^A$	>	a^D	d	u	U	d
a^A	<	a^D				
$2a^A$	=	a^D	d	E	U	d
$2a^A$	<	a^D	d	d	U	d
c^A		a^D	U	D	U	D
a^A		c^D	D	U	D	U
a^A		n^D	d	U	d	E
n^A		a^D	E	d	U	d

* the symbols u/U (up), d/D (down) and E (equal) denote the *observed* band intensity ($I_A^O \dots$) relative to the band intensity ($I_A^C \dots$) calculated for the same degree of LRO and zero SRO; upper and lower case qualitatively denote the relative sizes of the differences.

** c denotes clustering, n denotes no clustering, a denotes anticlustering; $>$, $=$ and $<$ denote the relative degree of clustering or anticlustering.

the observed ($I_A^O \dots$) and calculated ($I_A^C \dots$) band intensities to derive information on SRO in amphiboles.

SPECTRAL EXPRESSION OF SRO IN AMPHIBOLES

Consider the band assignments as given in Table 1. It should be noted that the aggregate intensity of certain combinations of bands are related to the site occupancies in the following way:

$$\begin{aligned} I_A^O + I_{B'}^O + I_{C'}^O &= x_{M(3)} \\ I_{B'}^O + I_{C'}^O + I_D^O &= y_{M(3)} \\ 2I_A^O + 2I_{B'}^O + I_{B'}^O + I_{C'}^O &= 2x_{M(1)} \\ I_{B'}^O + 2I_{C'}^O + I_{C'}^O + 2I_D^O &= 2y_{M(1)} \end{aligned} \quad (5)$$

Note that this equation holds only if there is no variation in molar absorptivity with band frequency *within a single sample*. As shown by DELLA VENTURA *et al.* (this volume), this condition holds for binary (Mg,Ni)- and (Mg,Co)-potassium-richterite solid solutions, and hence we can use equation (5) for these amphiboles. For a given state of LRO, SRO can only find its spectral expression within the constraints of equation (5); the band intensities will vary with different SRO, but the band-intensity *sums* in equation (5) are fixed by the state of LRO. With these constraints, we can now examine the effects of different sorts of SRO on the spectrum for a given state of LRO.

Let us first consider the total possible number of ways in which the band intensities can deviate from the band intensities expected for complete short-range disorder. There are four bands, and for each band there are three possibilities: (1) $I^O > I^C$; (2) $I^O = I^C$; (3) $I^O < I^C$; we will designate these as *U*, *E* and *D*, respectively. There are $3^4=81$ possible arrangements of the symbols $\{U,E,D\}$ taken four at a time; are all of these possible deviations from short-range disorder? The answer to this is no; there are various constraints on allowed combinations of these symbols. First, as the bulk composition of the crystal is fixed, any combination of symbols that would require a change in the composition of the crystal is forbidden. Thus any combination of symbols that does *not* include both *U* and *D* is forbidden (except for *EEEE*); of the 81 possible arrangements, 30 fall within this forbidden category. For the same reason, any combination of symbols that does *not* include both *U* and *D* in the first and in the last triplets of symbols is also forbidden; 26 arrangements fall within this category. This leaves 25 arrangements to consider.

Let each band differ by ΔI_i ($i = A \dots D$) from the values calculated for no short-range order (*i.e.*, $\Delta I_i = I_i^O - I_i^C$). The Mg and M^{2+} contents of the crystal are fixed, and hence

$$\text{for Mg: } 3\Delta I_A + 2\Delta I_B + \Delta I_C = 0 \quad (6.1)$$

$$\text{for } M^{2+}: \Delta I_B + 2\Delta I_C + 3\Delta I_D = 0 \quad (6.2)$$

Rearranging gives the following relationships:

$$\Delta I_B = \Delta I_D - 2\Delta I_A \quad (7.1)$$

$$\Delta I_C = \Delta I_A - 2\Delta I_D \quad (7.2)$$

Thus the variations in I_i^O relative to I_i^C must conform to the constraints of equation (7); this will be very important in associating specific band intensities with specific local arrangements. Inspection of the remaining 25 combinations of symbols shows that 8 are incompatible with equation (7), leaving 17 combinations that are possible (within the constraint of constant chemical composition).

MgMgMg and/or $M^{2+}M^{2+}M^{2+}$ clustering

Let us first consider the case of MgMgMg clustering. This will increase the relative intensity of the A band above the value of I_A^C given in equations (3) and (4). From equation (5)

$$\Delta I_A + \Delta I_{B'} + \frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) = 0 \quad (8.1)$$

$$\Delta I_A + \Delta I_{B'} + \Delta I_{C'} = 0 \quad (8.2)$$

With MgMgMg clustering, ΔI_A is positive, and hence equation (8) reduces to

$$\Delta I_{B'} + \frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) < 0 \quad (9.1)$$

$$\Delta I_{B'} + \Delta I_{C'} < 0 \quad (9.2)$$

However, there cannot be MgMgMg clustering ($\Delta I_A > 0$) without a compensating difference in the number of other configurations. We will examine this aspect of the problem next.

No $M^{2+}M^{2+}M^{2+}$ clustering. This condition means that $\Delta I_D = 0$; also, the state of LRO for M^{2+} is fixed, and hence

$$\begin{aligned} \frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) + \Delta I_{C'} + \Delta I_D &= \frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) \\ &+ \Delta I_{C'} = 0 \end{aligned} \quad (10.1)$$

$$\Delta I_{B'} + \Delta I_{C'} + \Delta I_D = \Delta I_{B'} + \Delta I_{C'} = 0 \quad (10.2)$$

Combining (9) and (10) gives $\Delta I_B < 0$ and $\Delta I_C > 0$. Thus for MgMgMg clustering with no $M^{2+}M^{2+}M^{2+}$ clustering (or anticlustering), $I_B^O < I_B^C$ and $I_C^O > I_C^C$. We may summarize this behaviour by the symbol *uDuE* (the size of the *U/u* and *D/d* symbols are a crude measure of the relative values of ΔI_i).

$M^{2+}M^{2+}M^{2+}$ clustering. This condition means that $\Delta I_D > 0$. As we are dealing with MgMgMg clustering, equation (9) holds. As we are dealing with $M^{2+}M^{2+}M^{2+}$ clustering,

$$\frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) + \Delta I_C < 0 \quad (11.1)$$

$$\Delta I_{B'} + \Delta I_{C'} < 0 \quad (11.2)$$

There are three distinct cases for MgMgMg clustering in combination with $M^{2+}M^{2+}M^{2+}$ clustering: MgMgMg clustering greater than ($\Delta I_A > \Delta I_D$), equal to ($\Delta I_A = \Delta I_D$) or less than ($\Delta I_A < \Delta I_D$) $M^{2+}M^{2+}M^{2+}$ clustering.

First we consider the case for MgMgMg clustering greater than $M^{2+}M^{2+}M^{2+}$ clustering: ($\Delta I_A > \Delta I_D$). The relations between ΔI_A and ΔI_D indicate that

$$|\Delta I_{B'} + \frac{1}{2}(\Delta I_{B'} + \Delta I_{C'})| > |\frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) + \Delta I_C| \quad (12.1)$$

$$|\Delta I_{B'} + \Delta I_{C'}| > |\Delta I_{B'} + \Delta I_{C'}| \quad (12.2)$$

In this case, we may subtract equation (11) from equation (9) [2.(9.1)–(11.2)] to show that $\Delta I_B < 0$. Similarly, we can show that $\Delta I_B + \Delta I_C < 0$ but we cannot explicitly determine ΔI_C in this case [relationship (12) does not allow us to subtract (9.2) from 2.(11.1) as we have no knowledge of the relative magnitudes of the terms in each equation]. So we may temporarily represent this behaviour by the symbol UD^*u . To determine the * symbol, consider equation (7.2): $\Delta I_C = \Delta I_A - 2\Delta I_D$. As $\Delta I_A > \Delta I_D$, $\Delta I_C > 0$ if $\Delta I_A > 2\Delta I_D$; $\Delta I_C = 0$ if $\Delta I_A = 2\Delta I_D$; $\Delta I_C < 0$ if $\Delta I_D < \Delta I_A < 2\Delta I_D$. These conditions correspond to the symbols $UDuu$, $uDEu$ and $uDdu$, respectively. Thus MgMgMg clustering greater than $M^{2+}M^{2+}M^{2+}$ clustering has three different spectral expressions, depending on the relative amount of clustering in each case.

Next consider the case for MgMgMg clustering equal to $M^{2+}M^{2+}M^{2+}$ clustering: ($\Delta I_A = \Delta I_D$), and hence the $>$ signs in relation (12) become = signs. Expressions (9) and (11) reduce to $\Delta I_B = \Delta I_C$. Combination of this relation with equation (7) indicates that $\Delta I_B = \Delta I_C < 0$. These conditions correspond with the symbol $UDDU$.

Last, consider the case of MgMgMg clustering less than $M^{2+}M^{2+}M^{2+}$ clustering. This case is symmetrically related to the case of MgMgMg clustering greater than $M^{2+}M^{2+}M^{2+}$ clustering, and the solutions follow directly: $uuDU$, $uEDu$ and $udDu$. All of these configurations and their spectral expression as quartets of symbols are listed in Table 2.

MgMgMg and $M^{2+}M^{2+}M^{2+}$ anticlustering

These arrangements are symmetrically related to the cases involving clustering derived in detail

above. Hence the arrangements may be derived directly from the algebraic symmetry of the equations. All distinct configurations and their spectral expression are listed in Table 2.

Clustering in combination with anticlustering

The combination of clustering of one component (*e.g.*, Mg) with anticlustering of another (*e.g.*, M^{2+}) is somewhat different from combinations involving only clustering or only anticlustering. This arises because ΔI_A and ΔI_D have different signs in equations (8) and (10), and hence the relative complexities involving whether or not ΔI_A is less than, equal to or greater than $2\Delta I_D$ [equation (7)] do not arise.

Consider first the case where MgMgMg clustering is greater than or equal to $M^{2+}M^{2+}M^{2+}$ anticlustering: $\Delta I_A > 0$, $\Delta I_D < 0$, $|\Delta I_A| \geq |\Delta I_D|$. Equation (11) becomes

$$\frac{1}{2}(\Delta I_{B'} + \Delta I_{C'}) + \Delta I_C > 0 \quad (13.1)$$

$$\Delta I_{B'} + \Delta I_{C'} > 0 \quad (13.2)$$

Relation (12) holds (as \geq rather than $>$), and we may combine expressions (9) and (11) to show that $\Delta I_B < 0$ [2.(9.1) – 11.2], giving rise to the symbol UD^*D ; we cannot derive an analogous expression for ΔI_C under the conditions of relation (12). From equation (7.2), $\Delta I_C > 0$ as $\Delta I_A > 0$ and $\Delta I_D < 0$, and hence the general symbol is $UDUD$.

For $\Delta I_A > 0$, $\Delta I_D < 0$, $|\Delta I_A| < |\Delta I_D|$, expressions (9) and (11) combine to show that $\Delta I_C > 0$ [2.(11.1) – (9.2)], and equation (7.1) gives $\Delta I_B < 0$ for the same general symbol $UDUD$.

The arguments for MgMgMg anticlustering combined with $M^{2+}M^{2+}M^{2+}$ clustering are symmetrical with regard to those given above, and the general symbol for this behaviour is thus $DUDU$.

VARIATION IN TRANSITION PROBABILITY WITH ABSORPTION ENERGY

All earlier work implicitly assumed that the transition moment was the same for all of the different bands in the OH-stretching spectra of complex amphiboles. It now seems that this may not be the case. In a polarized single-crystal absorption study of amphiboles, SKOGBY and ROSSMAN (1991) showed that the integrated molar absorptivity for the principal OH-stretching band increases with decreasing stretching frequency. This is also the same for vesuvianite (GROAT *et al.*, 1995) in which the range in OH-stretching frequency is much greater than in amphibole. Also, BURNS and HAWTHORNE (1994) have shown the analogous relation for normalized OH-stretching-band intensities in powder infrared spectra of borate minerals. Thus there is not

a 1:1 correspondence between the intensity of OH-stretching absorption bands and the relative abundance of short-range configurations with which they are associated. This relationship must be characterized and the measured intensities of the absorption bands must be corrected for this phenomenon before any effects of SRO can be examined.

DELLA VENTURA *et al.* (this volume) consider this problem for synthetic (Ni,Mg,Co)-potassium-richterite and show that the curve of SKOGBY and ROSSMAN (1991) is *not* compatible with the variation in relative band intensities as a function of composition [at the M(1) and M(3) sites] as measured by Rietveld refinement. Preliminary spectra on other synthetic amphibole series indicate that a variety of behaviour may occur with regard to variation in molar absorptivity as a function of band frequency. However, the arguments of DELLA VENTURA *et al.* (this volume) suggest that this problem is susceptible to solution for many amphibole series of interest. This being the case, the equations given here allow characterization of SRO over the M(1) and M(3) sites.

Acknowledgements—We thank M. R. Raudsepp and an anonymous referee for their comments. FCH was supported by a Killam Fellowship and by Operating, Infrastructure and Equipment grants from the Natural Sciences and Engineering Research Council of Canada.

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