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Lattice vibrations in relatively complicated crystal structures: Aragonite

U. A. Jayasooriya and S. F. A. Kettle

School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom

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The observation that the aragonite structure [P_{nma} (D_{2h}^{16})] is a distortion of a more symmetrical structure [$P_{\bar{3}m1}$ (D_{3d}^{3})] provides, for compounds crystallizing with this lattice, a symmetry-based model for the assignment of the lattice vibrations at $\vec{k} \approx \vec{0}$ in which band intensity is used as an assignment criterion.

Despite the considerable instrumental and theoretical advances of recent years there are many aspects of the vibrational spectra of even simple species which are the subject of debate. While this statement is often true for internal mode spectra it is even more applicable to the lattice mode region. The difficulty is that of the need for a model. A common pattern is that a mathematical model of intermolecular potentials is presented which, perhaps by an iterative procedure, leads to lattice mode frequencies which are compared with experimental values. This means that for all but very simple systems different models can, and do, lead to rather different assignments of the observed features. In this situation it is desirable to have a clear physical model since such a model should provide assignments which are ostensibly independent of a particular mathematical approach. Unfortunately, such physical models are not generally available. In the present paper we seek to remedy this situation by providing a symmetry-based model which gives a good qualitative interpretation of the lattice mode vibrational spectra of KNO_3(II), the phase stable at room temperature, and the isomorphic species aragonite, $CaCO_3$. Perhaps not surprisingly, our assignments differ from all of those currently in the literature.

The present work is based on an earlier publication[1] in which we have proposed a simple model to explain the peculiar intensity distributions of the internal vibration spectra of KNO_3(II). This model is based on the recognition that the actual crystal lattice of KNO_3(II)—P_{nma} with $Z=4$—represents a small distortion of a higher symmetry lattice, $P_{\bar{3}m1}$, containing only two molecules in the unit cell (Fig. 1). The observed internal mode spectra are, then, essentially, those expected for the latter space group.

The generality of the application of these predictions to other compounds with the aragonite crystal structure was demonstrated using the (limited) vibrational data available in the literature.[2] In the present paper we extend the above model to the lattice region spectra. Of the large number of compounds possessing the aragonite lattice, the greatest amount of vibrational data have been reported for phase II potassium nitrate[3–5] and for aragonite[6,7] itself. These two compounds are therefore used in the present paper to test the applicability of the model we present. The available Raman data of both species are of a much higher quality than the infrared and so in the present work we shall concentrate on the former. Subsequently we shall make predictions for the infrared; although the available data do not enable our infrared predictions to be fully tested, they are in full agreement with such data as are available.

Lattice region vibrational spectroscopic data for KNO_3 phase II have been reported by many workers. Brooker[3] and Akiyama *et al.*[4] obtained excellent single-crystal Raman spectra which are in good agreement with each other. Far-infrared spectra have been reported by Haider and Happ[5] using single crystals and the asymmetric Fourier spectroscopic technique. Just as the number of bands reported in the internal mode spectra appeared to be too few so, too, there are fewer features in the lattice mode region than expected for a factor group analysis based on P_{nma} (D_{2h}^{16}). Brooker[3] observed only 13 bands (even after cooling to 77 K) in the lattice region of the Raman spectrum of KNO_3(II) although 18 are predicted. Similarly, in the far-infrared spectrum of KNO_3(II) some predicted bands do not appear. Lattice mode ir and Raman spectral data on $CaCO_3$ (aragonite) have been reported by Frech *et al.*[7] who also provide a brief but useful review of the litera-

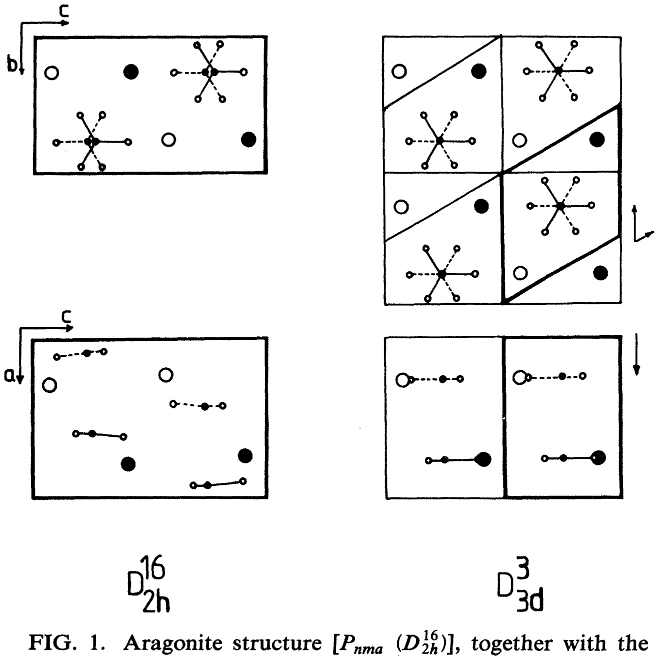

FIG. 1. Aragonite structure [P_{nma} (D_{2h}^{16})], together with the more symmetrical structure obtainable by a slight distortion [$P_{\bar{3}m1}$ (D_{3d}^{3})].

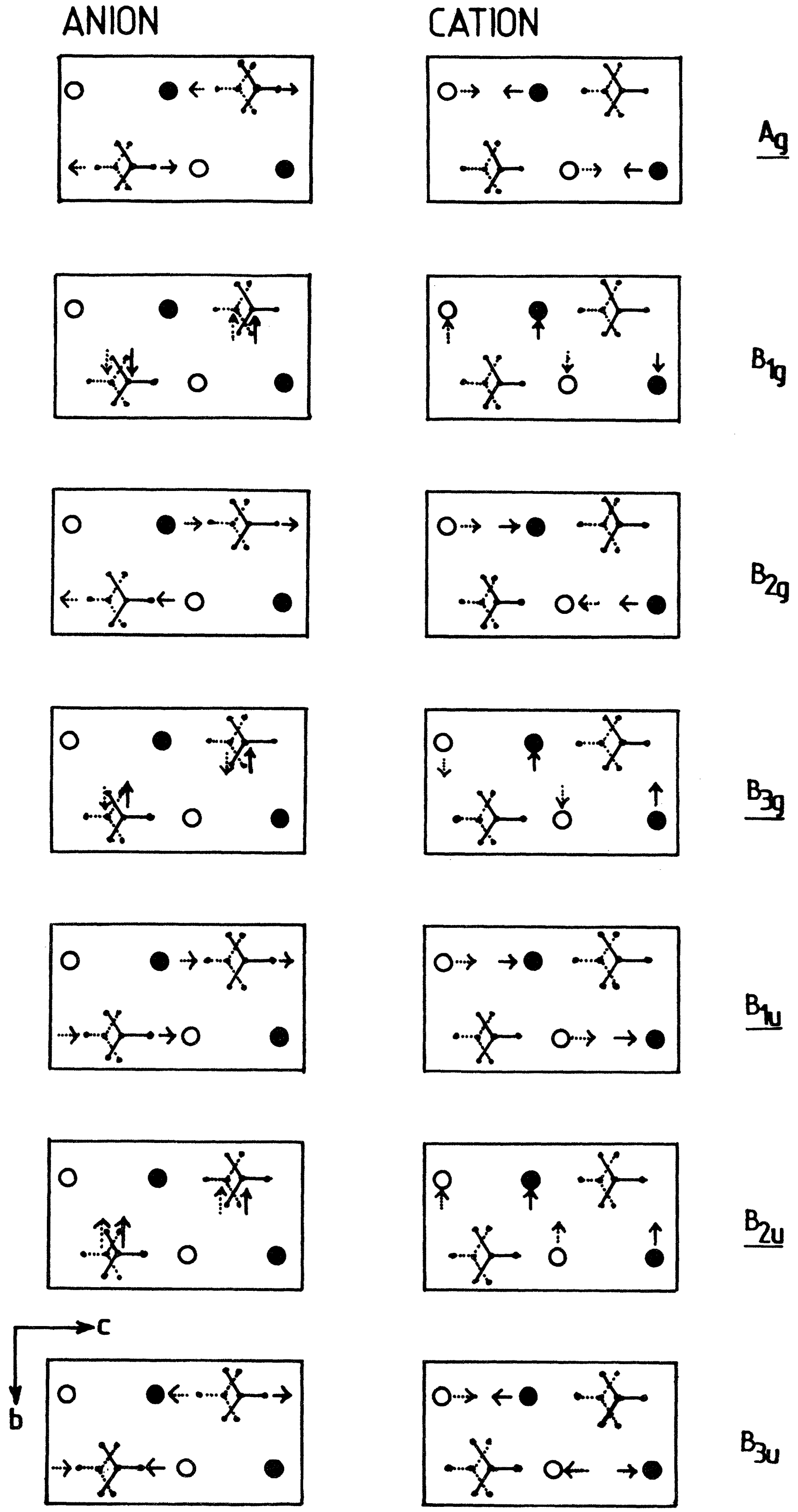

FIG. 2. Symmetry coordinates of the translational lattice modes in the (*b*,*c*) plane. The coordinates underlined are those for which adjacent unit cells in the higher symmetry lattice vibrate in-phase and so are expected to correspond to strong spectral features.

ture. In the Raman study, the intensity patterns are quite similar to those observed in the case of potassium nitrate II with several bands of very low intensity and some unobserved. In their single-crystal Raman study of aragonite, Frech *et al.*[7] used the standard setting [i.e., P_{nma} (D_{2h}^{16})] while Brooker and Akiyama *et al.* in their work on KNO_3 used the nonstandard setting adopted in the x-ray crystallographic study [i.e., P_{mcn} (D_{2h}^{16})].[8] These differences give rise to the use of different symmetry labels in single-crystal Raman work. In the present paper we use the standard setting, P_{nma}, and refer all data to it.

In an earlier publication[1] the near existence of a threefold axis in the aragonite lattice was used to explain the relative intensities of bands associated with the internal vibrations of KNO_3(II). In this model a slight distortion of the aragonite structure gives a space group with trigonal symmetry, $P_{\bar{3}m1}$ (D_{3d}^3) with $Z=2$. For aragonites rather small displacements perpendicular to the a axis (Fig. 1) and larger displacements parallel to the a axis are needed to create the crystallographic threefold axis. The form of the vibrational symmetry coordinates of the internal modes is independent of both these translations and so it was possible to neglect the latter when considering the relative intensities of internal modes. In external lattice modes, however, it is the interionic potential which is being vibrationally explored and so we would not expect it to be generally permissable to neglect translational differences. Not surprisingly, then the direct application of our model fails to explain the external mode spectra. However, once the source of the weakness is located, it is possible to modify the model and, thereby, to obtain one which predicts the relative intensities of bands associated with lattice modes. This, in turn, leads to a unique assignment of the observed spectral features.

Because of the D_{2h}^{16} symmetry, the lattice modes of crystals with the aragonite structure are quantized along three orthogonal directions. Our idealized D_{3d}^3 model differs from the D_{2h}^{16} by a small translational displacement along the c axis but with no translational displacements along the b axis. We therefore expect that as a first approximation, the D_{3d}^3 model should be valid with respect to these two axes. In contrast, the D_{3d}^3 and D_{2h}^{16} models of the structure differ by relatively large translations along a and we cannot expect similar predictions to arise from them. We therefore separate the lattice problem into two parts. Those vibrational modes associated with motions parallel to the b and c axes are determined using the D_{3d}^3 model while those associated with the a axis are determined using the actual D_{2h}^{16} structure.

It is to be recalled that it is only vibrations with $\vec{k} \simeq \vec{0}$ which may be investigated by infrared and Raman techniques. That is, the only motions of units related by pure translations which are spectrally active will involve in-phase motions of these units. This has an important consequence for motions parallel to the (a,b) plane for in this plane the D_{3d}^3 unit cell is one-half the size of the D_{2h}^{16}. That is, to a first approximation, only in-phase motions of the two D_{3d}^3 cell components will have significant intensity in D_{2h}^{16}. This is formally rather similar to the requirement that factor group analyses relate to a primitive unit cell when the crystallographic work is more conveniently

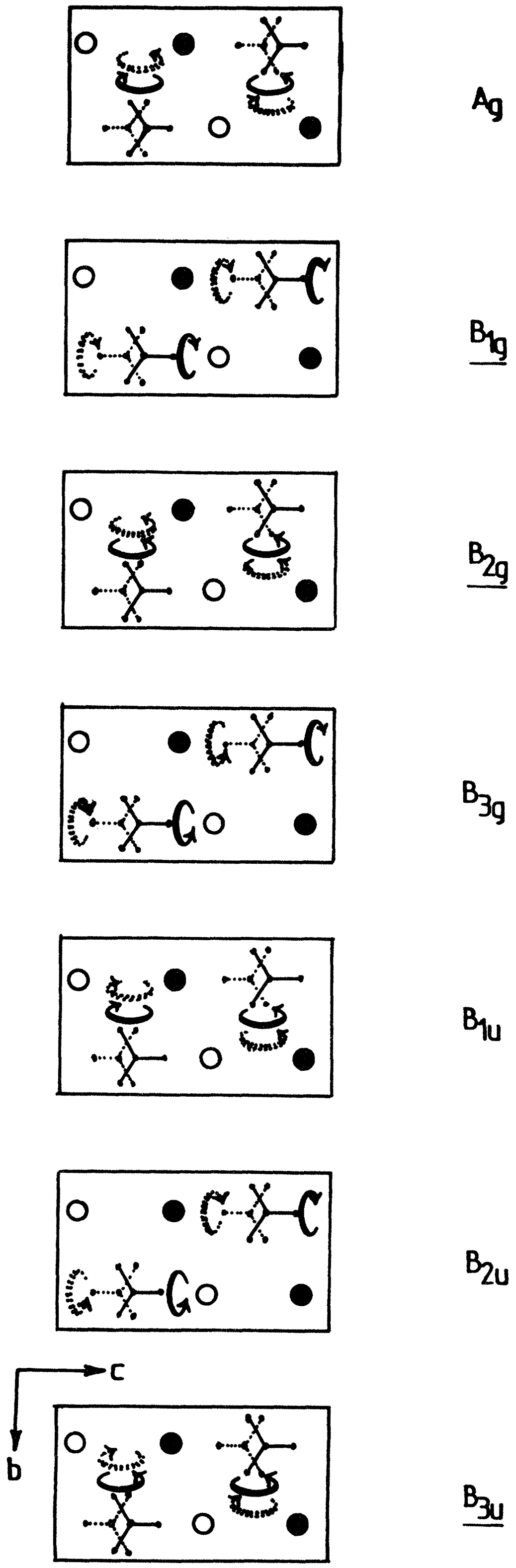

FIG. 3. Symmetry coordinates of the rotatory lattice modes about b and c axes. The coordinates underlined are those for which adjacent unit cells in the higher-symmetry lattice vibrate in phase and so are expected to correspond to strong spectral features.

carried out in a nonprimitive, centered unit cell. In D_{2h}^{16} the four K^+ and four NO_3^- units give rise to the following translations in the (b,c) plane:

$$2A_g+2B_{1g}+2B_{2g}+2B_{3g}+2A_u+2B_{1u}+2B_{2u}+2B_{3u}\ ,$$

from which we delete $B_{1u}+B_{2u}$, two acoustic modes with zero frequency at $\vec{k}\simeq\vec{0}$. The A_u modes are inactive in both infrared and Raman. This leaves

$$2A_g+2B_{1g}+2B_{2g}+2B_{3g}+B_{1u}+B_{2u}+2B_{3u}$$

as potentially spectrally visible species, eight Raman and four infrared active.

In Fig. 2 we show schematically the cation and anion symmetry coordinates which must be combined to obtain the normal coordinates corresponding to those factor group species (in each case both in-phase and out-of-phase combinations of cation and anion motions must be taken). From the symmetry coordinates shown in Fig. 2 we now select those which are translationally invariant ($\vec{k}\simeq\vec{0}$) for the D_{3d}^{3} unit cell (and so are those which are expected to show pronounced spectral activity in D_{2h}^{16}). These modes are indicated in Fig. 2 and have symmetry A_g, B_{3g}, B_{1u}, and B_{2u}. The modified spectral predictions are therefore for four Raman ($2A_g+2B_{3g}$) and two infrared ($B_{1u}+B_{2u}$) bands associated with translations parallel to b and c. Rotations about axes parallel to b and c are similarly treated. For these the D_{2h}^{16} factor group model leads to the species

$$A_g+B_{1g}+B_{2g}+B_{3g}+A_u+B_{1u}+B_{2u}+B_{3u}\ ,$$

from which the spectrally inactive A_u may be deleted. Figure 3 shows that from the remainder the D_{3d}^{3} translational invariance requirement selects the B_{1g}, B_{2g}, and B_{3u} modes as potentially spectrally active.

To these b and c axis motions have to be added those of translations (T_a) and (R_a) rotations associated with the a axis. After deletion of A_u and acoustic modes these transform as $2A_g+2B_{2g}+2B_{1u}+B_{3u}$ (T_a) and $B_{1g}+B_{3g}+B_{2u}$ (R_a). Combining all together we obtain for the predicted Raman spectrally active vibrations

$$4A_g+2B_{1g}+3B_{2g}+3B_{3g}\ ,$$

and for the infrared,

$$3B_{1u}+2B_{2u}+2B_{3u}\ .$$

One further simplification is immediately possible within our model. This arises from the fact that in the D_{3d}^{3} group a rotation about the threefold axis, a motion located in the (b,c) plane, tranforms as A_{2g}, a symmetry species which is infrared and Raman silent. We therefore expect that the corresponding motions in D_{2h}^{16} will have little spectral activity, and delete the modes $B_{1g}+B_{3g}+B_{2u}$, from our predicted spectra, leaving for the Raman

$$4A_g+B_{1g}+3B_{2g}+2B_{3g}\ ,$$

and for the infrared,

$$3B_{1u}+2B_{3u}+B_{2u}\ .$$

Before comparing these predictions with literature data one further comment about relative Raman intensities is

TABLE I. Frequency and qualitative intensity data.

Mode	Strong features		Weak features		Assignment
	$CaCO_3$	KNO_3	$CaCO_3$	KNO_3	
A_g	142	54			T_a anion
	161	80			T_a cation
			193	75	R_b anion
	214	107			T_c anion
	284	140			T_c cation
B_{1g}			112	104	R_a anion
	152	83			R_c anion
				50	breakthrough B_{3g}
				124	
B_{2g}				83	breakthrough B_{1g}
				50	breakthrough B_{3g}
	180	67			T_a anion
	206	135			R_b anion
	248	150			T_a cation
			260		
B_{3g}				123	R_a anion
	190	51			T_b anion
			206		breakthrough B_{2g}
	272	83			T_b cation
Predictions:	decomposition (full factor group)		$5A_g+4B_{1g}+5B_{2g}+4B_{3g}$		
	our model		$4A_g+B_{1g}+3B_{2g}+2B_{3g}$		

appropriate. We are concerned with the changes in (unit cell) polarizability consequent upon translational and rotational motions of its constituent ions. It seems qualitatively reasonable that these changes should be greater the larger the net negative (or smaller the net positive) charge of an ion, *mutatis mutandis.* We therefore anticipate that the polarizability changes associated with the $CO_3{}^{2-}$ ion to be much greater than that of the isoelectronic $NO_3{}^{-}$ ion. Similarly, motion of the K^+ ion would be expected to be associated with higher polarizability changes than Ca^{2+}. Such differences in polarizability associated with individual ions will be reflected in the vibrational intensities in the Raman. For vibrations involving both the cation and the anion, these will have an averaging effect on the net polarizability changes and thus should have comparable intensities in both KNO_3 and $CaCO_3$. However, rotational modes involving only the anion would be expected to show marked differences in intensity.

We are now able to qualitatively apply our model to the single-crystal Raman spectra. Strong peaks are expected to be distributed $4A_g+B_{1g}+3B_{2g}+2B_{3g}$; weaker peaks may be associated with "forbidden" modes on our model, breakthrough from strong bands of other polarizations, or anharmonic features. A comparison of the relative intensities of corresponding bands in KNO_3 and $CaCO_3$ spectra should indicate their motional parentage.

Frequency and qualitative intensity data are reported in Table I, from which it is evident that the number and distribution of strong features is entirely in accord with the predictions of our model. Further, a more detailed study of band intensities reveals patterns which are explicable in terms of the mixed factor group model presented in this paper.

Of the observed strong modes the single B_{1g} is of particular interest. The published spectra suggest that this band has an enhanced intensity in $CaCO_3$ compared to that in KNO_3. This is entirely understandable for a mode which involves anion rotation (Fig. 3). We are thus led to an assignment which agrees with that of Akiyama *et al.*[4]; the assignment of this B_{1g} mode to the rotation of the $NO_3{}^{-}$ about the *c* axis in KNO_3, but note that it is in disagreement with its assignment for $CaCO_3$ in the literature.[7]

Of the three strong B_{2g} modes predicted on our model, one is largely a rotation of the anion about the *b* axis, while the other two involve cation and anion translations along the *a* axis. A comparison of the intensities of the B_{2g} modes reported for KNO_3 and $CaCO_3$ immediately shows, in the case of $CaCO_3$, one mode to be much more intense, while in KNO_3 all are of similar intensities. This is understandable on our model because one B_{2g} mode is largely associated with the rotation of the anion about the *b* axis and should be much stronger with the more polarizable $CO_3{}^{2-}$ ion than for the $NO_3{}^{-}$. The other two B_{2g} bands are, then, assigned to modes which are largely translations along the *a* axis. Similarly, on our model the two strong B_{3g} vibrations are assigned to translational motions parallel to *b*. These assignments are in disagreement with those in the literature.

A comparison of the A_g features in the spectra of the two salts shows a strong band in the $CaCO_3$ spectrum at $\sim 214\ cm^{-1}$ which would be appropriately assigned to a mode which is largely anion translation parallel to the *c* axis and to correspond to the relatively weaker mode at $107\ cm^{-1}$ in KNO_3. Similarly, we can assign the mode at $142\ cm^{-1}$ in $CaCO_3$ ($54\ cm^{-1}$ in KNO_3) to anion translation parallel to the *a* axis. The weak feature at $\sim 193\ cm^{-1}$ we assign as largely a rotation about axes parallel to *b*, a mode which is forbidden in our model.

The limited amount of far-infrared work reported in the literature is in agreement with our predictions that at least one mode belonging to each symmetry species is too weak to observe. The predictions of our model are for modes of $3B_{1u}+B_{2u}+2B_{3u}$ symmetries. These are to be compared with the D_{2h}^{16} factor group predictions of $4B_{1u}+3B_{2u}+4B_{3u}$. In fact one asymmetric broad band with a halfwidth of $75\ cm^{-1}$ is found for each symmetry species in the reflection infrared spectra of a single crystal of KNO_3(II). Clearly the breadth of the observed bands precludes any meaningful analysis. However, it may be that it is the opposed translationary motions of the oppositely charged ions that makes the major contribution to the dipole moment change and leads to a single band being dominant in each spectrum.

In the present paper we provide a symmetry-based assignment of the lattice region which provides an independent check of lattice mode calculations. It is significant that our assignments are often in disagreement with those reported in the literature and may indicate that the inherent limitations on assumed potential parameters are greater than sometimes supposed.

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[1] M. Ismail, U. A. Jayasooriya, and S. F. A. Kettle, J. Chem. Phys. (in press).

[2] M. Ismail, U. A. Jayasooriya, and S. F. A. Kettle, J. Mol. Struct. 79, 349 (1982).

[3] M. H. Brooker, Can. J. Chem. 55, 1242 (1977).

[4] K. Akiyama, Y. Morioka, and I. Nakagawa, J. Phys. Soc. Jpn. 48, 898 (1980).

[5] G. Haider and H. Happ, J. Phys. Chem. 12, 1011 (1979).

[6] A. Yamamoto, Y. Shiro, and H. Murata, Bull. Chem. Soc. Jpn. 47(2), 265 (1974).

[7] R. Frech, E. C. Wang, and J. B. Bates, Spectrochim. Acta, Part A 36, 915 (1980).

[8] J. K. Nimmo and B. W. Lucas, Nature Phys. Sci. 237, 61 (1972).