

CHARACTERIZATION AND ASSIGNMENT OF FAR INFRARED ABSORPTION BANDS OF K⁺ IN MUSCOVITE

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Abstract—To assign far infrared (FIR) absorption bands of K⁺ in muscovite, dichroic experiments were performed. For a muscovite crystal rotated about a crystallographic axis, c^* , a , or b , two bands corresponding to vibration modes of K⁺ appear, respectively, at 107 and 110 cm⁻¹ (rotation about c^*), 107 and 143 cm⁻¹ (rotation about a), and 110 and 143 cm⁻¹ (rotation about b). Two in-plane modes at 107 and 110 cm⁻¹ and one out-of-plane mode at 143 cm⁻¹ are identified for the vibrations of K⁺ in muscovite. Each of these transition moments are near the crystallographic axes b , a , and c , respectively. These observations match well predictions based on the approximate C_3 , symmetric environment of K⁺, although the site symmetry in the space group of muscovite is only C_2 .

Key Words—Dichroism, Far Infrared, Muscovite, Potassium, Transition Moment, Vibration Mode.

INTRODUCTION

One of the first papers on the far infrared (FIR) absorption bands of K⁺ in micas was published by Ishii *et al.* (1967). Tateyama *et al.* (1977) showed a negative linear relationship between the frequency, σ (cm⁻¹), of compensating cations and the distance between the cation, M⁺, and the proximal oxygen atoms of the ditrigonal tetrahedral cavity, $d_{(M-O)_{\text{inner}}}$. Fripiat (1981) reported the relationship between the frequency, σ (cm⁻¹), and $\sqrt{Z/M}$ where Z and M are, respectively, the charge and the mass of compensating cations. Schroeder (1990) and Prost and Laperche (1990) independently assigned the FIR absorption band near 100 cm⁻¹ to K⁺ in micas. Laperche (1991) and Laperche and Prost (1991) exchanged K⁺ of micas by other cations and again assigned the FIR absorption bands near 100 and 140 cm⁻¹ to the vibration of the compensating cations.

In their paper, Ishii *et al.* (1967) suggested four modes of vibration of K⁺ in muscovite. Mode III was assigned to the deformation of the double ditrigonal ring which forms the cage around K⁺. Farmer (1974a) wrote “the in-plane vibrations of K⁺ in micas give medium intensity bands near 100 cm⁻¹, the corresponding out-of-plane vibrations lie near 150 cm⁻¹” suggesting only modes of vibration parallel and perpendicular to the (001) plane of the structure. Fripiat (1981) also refers to the in-plane and out-of-plane vibrations of compensating cations. Laperche and Prost (1991) failed to properly assign the modes I and II described by Ishii *et al.* (1967). The aim of this paper is to determine the band assignments by the study of the in-plane and out-of-plane dichroic character of FIR absorption bands of K⁺ in muscovite.

MATERIAL AND METHOD

A muscovite crystal whose a and b axes were determined with a polarizing microscope was used. A polarizer fixed the direction of the electric field \vec{E} of the FIR radiation in the incidence plane, which is horizontal (Figure 1). Three experiments were performed corresponding to the rotation of the muscovite crystal about c^* [*i.e.*, normal to the (001) plane], a , and b . The in-plane rotation experiments about c^* and the out-of-plane rotation experiments about a and b were performed by rotating the crystal 360° about each axis (Figure 1). The components of the transition moment \vec{m} involved in each rotation are, respectively, $\vec{m}_{(b,c^*)}$, $\vec{m}_{(a,c^*)}$, and $\vec{m}_{(a,b)}$ (the projection of \vec{m} on the plane perpendicular to the rotation axis). The three experiments were performed with the rotation axis perpendicular to \vec{E} . The angle of rotation, ϕ , is the angle a or b makes with \vec{E} . For the rotation about c^* and a , $\phi = 0^\circ$ where b is parallel to \vec{E} (Figure 1a and 1b). For the rotation about b , $\phi = 0^\circ$ where a is parallel to \vec{E} (Figure 1c). Experimental data between 60–120° were not collected when out-of-plane dichroic measurements were performed.

RESULTS

Figure 2 gives the FIR spectra between 30–230 cm⁻¹ as a function of the angle of rotation, ϕ , of the muscovite crystal about the c^* axis. A small but reproducible shift from 107 to 110 cm⁻¹ is observed as the angle between the electric field \vec{E} of the FIR radiation and the axis b increases from 0 to 90° and a shift from 110 to 107 cm⁻¹ occurs when ϕ increases from 90 to 180°. To explain this shift, two bands at 107 and 110 cm⁻¹ are considered (see below) for K⁺ in muscovite. Note in Figure 2 that the intensity of the

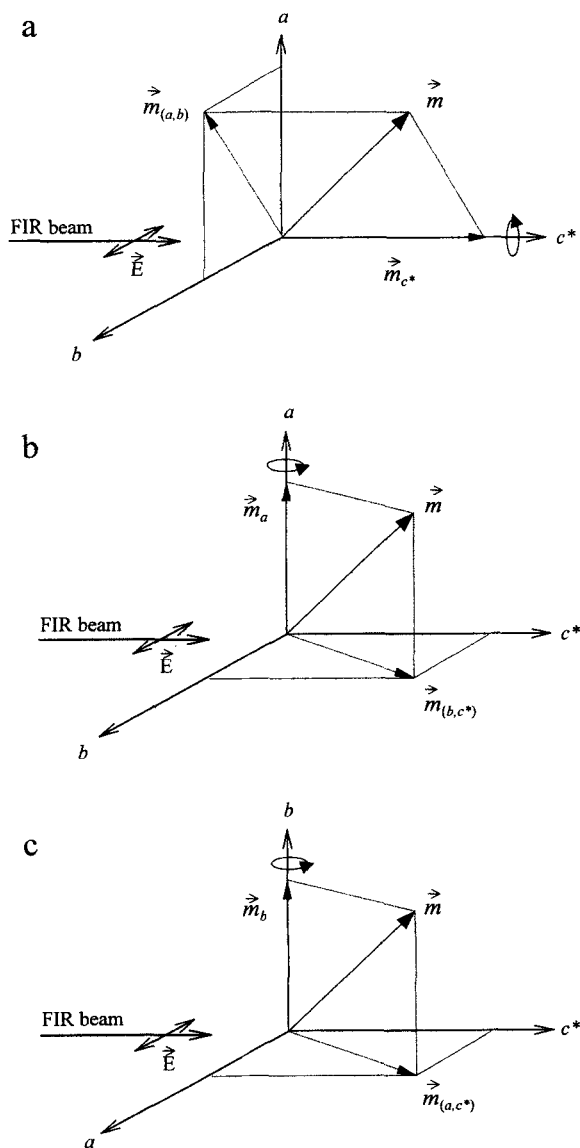


Figure 1. Relationships of the crystallographic axes of muscovite with respect to \vec{E} . (a) rotation about c^* , in-plane dichroic character. Out-of-plane dichroic character shown for (b) about a and (c) about b . The angle of rotation, ϕ , is the angle \vec{E} makes with a or b .

165- cm^{-1} band remains constant as the crystal is rotated about c^* , but the 187- cm^{-1} band intensity minimizes at 90° and maximizes at 0° and 180° .

Figure 3 gives the FIR spectra of muscovite as a function of the angle of rotation, ϕ , about a . The 107- cm^{-1} band does not shift but its intensity changes slightly. The intensity of an absorption band at 143 cm^{-1} [not seen in the first series of experiments (Figure 2)] increases and decreases as a function of ϕ . The 164- and 187- cm^{-1} bands are unaffected by the rotation of the muscovite crystal about a . Thus, the out-

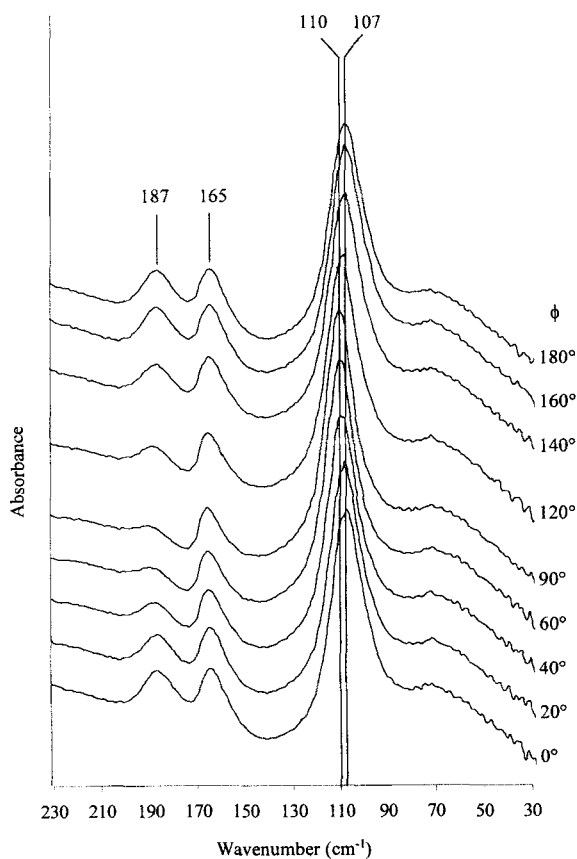


Figure 2. FIR spectra of a muscovite crystal rotated about the c^* axis. ϕ corresponds to the angle between \vec{E} and b .

of-plane dichroic experiment about a shows also the existence of two absorption bands for K^+ in muscovite at 107 and 143 cm^{-1} .

Figure 4 gives the FIR spectra of muscovite as a function of the angle of rotation, ϕ , about b . The 110- cm^{-1} band remains fixed in the spectrum but its intensity changes slightly. The intensity of the 143- cm^{-1} band increases and decreases as ϕ changes. The intensity of the 190- cm^{-1} absorption band is also affected by the rotation about b . Thus, the out-of-plane dichroic experiment about b shows the existence of two absorption bands at 110 and 143 cm^{-1} for K^+ in muscovite.

DISCUSSION AND CONCLUSIONS

Laperche and Prost (1991) showed that K^+ in muscovite produces absorption bands near 110 and 140 cm^{-1} . The present pleochroic study of the FIR absorption bands of K^+ in muscovite shows the existence of three dichroic bands at 107, 110, and 143 cm^{-1} . For a muscovite flake rotated about either c^* , a , or b , only two bands occur, respectively, at 107 and 110 cm^{-1} , 107 and 143 cm^{-1} , or 110 and 143 cm^{-1} . The inability to observe a vibration mode when the muscovite crys-

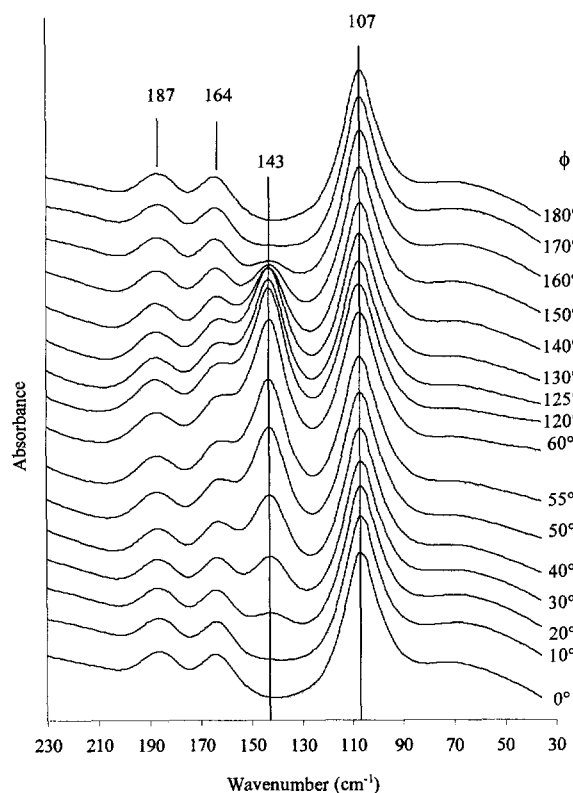


Figure 3. FIR spectra of a muscovite crystal rotated about the *a* axis. ϕ corresponds to the angle between \vec{E} and *b*.

tal is rotated about a crystallographic axis perpendicular to the electric field \vec{E} , implies that this vibration mode is parallel to the rotation axis. Thus, the out-of-plane vibration mode is perpendicular to the (001) plane and both in-plane vibration modes are, respectively, perpendicular to the (100)* and (010) planes. In other words, the transition moments $\vec{m}_{143 \text{ band}}$, $\vec{m}_{107 \text{ band}}$, and $\vec{m}_{110 \text{ band}}$ are parallel to the *c**, *b*, and *a* axes, respectively.

To obtain a more precise orientation of the vibration modes of K⁺ in muscovite, intensities were plotted versus ϕ about the *a*, *b*, and *c** axes.

The in-plane dichroic character: rotation about *c**

A shift was observed from 107 to 110 and to 107 cm⁻¹ as the muscovite crystal is rotated about *c** from 0 to 180° (Figure 2). A mathematical decomposition, assuming two components at 107 and 110 cm⁻¹, was made to quantify the intensity of each band as a function of the rotation angle. The decomposition was made with the Opus software developed by Bruker, Inc. (Wissembourg, France). The band profile, the bandwidth, and the position remain identical for all decompositions. Figure 5 gives the integrated intensity of the 107- and 110-cm⁻¹ bands versus ϕ about *c**, and similar plots are shown for *a* (Figure 6) and *b*

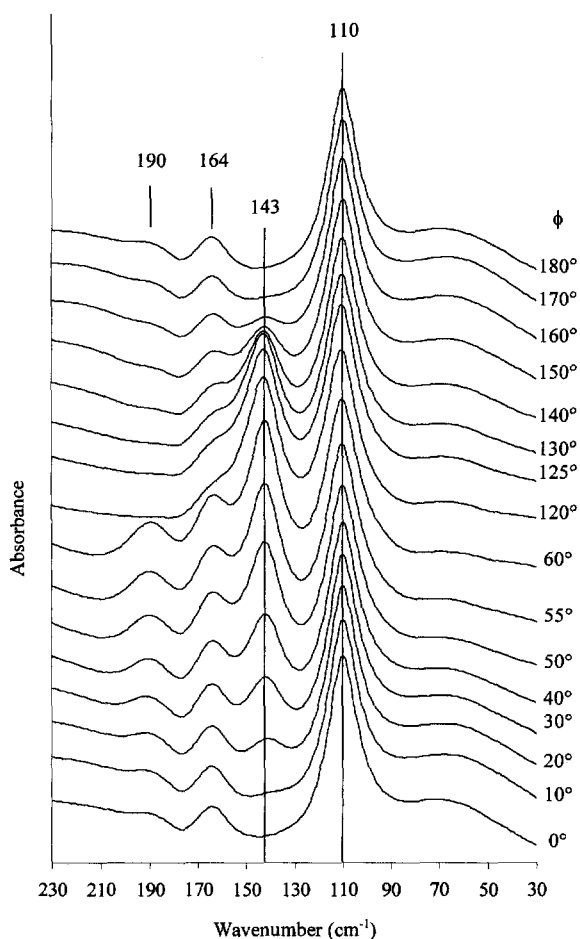


Figure 4. FIR spectra of a muscovite crystal rotated about the *b* axis. ϕ corresponds to the angle between \vec{E} and *a*.

(Figure 7). Calculated curves were obtained by considering that absorption-band intensity is a function of $I_{\text{max}} \cos^2 \phi$, where I_{max} is the maximum intensity of $\vec{m}_{107 \text{ band}}$ and $\vec{m}_{110 \text{ band}}$ and ϕ is the angle of rotation between *b* and the electric field \vec{E} . I_{max} is calculated by determining the slope of the plot of the intensity *I* of $\vec{m}_{107 \text{ band}}$ and $\vec{m}_{110 \text{ band}}$ versus $\cos^2 \phi$. The fit between experimental and calculated data is excellent. Note that $\vec{m}_{107 \text{ band}}$ and $\vec{m}_{110 \text{ band}}$ are perpendicular. The maximum of the intensity occurs where $\vec{m}_{107 \text{ band}}$ and $\vec{m}_{110 \text{ band}}$ are parallel to \vec{E} (Figure 8a).

The out-of-plane character: rotation about *a* or *b*

Only absorption bands at 107 and 143 cm⁻¹ are visible in the (100)* plane for rotation about *a* (Figure 3). The intensities of both bands are plotted versus ϕ in Figure 6. The calculated values fit the experimental data well in the case of the 143-cm⁻¹ band, but not for the 107-cm⁻¹ band. However, the refraction angle and the optical path were not considered. Nevertheless, the maximum intensity of the 107-cm⁻¹ band occurs

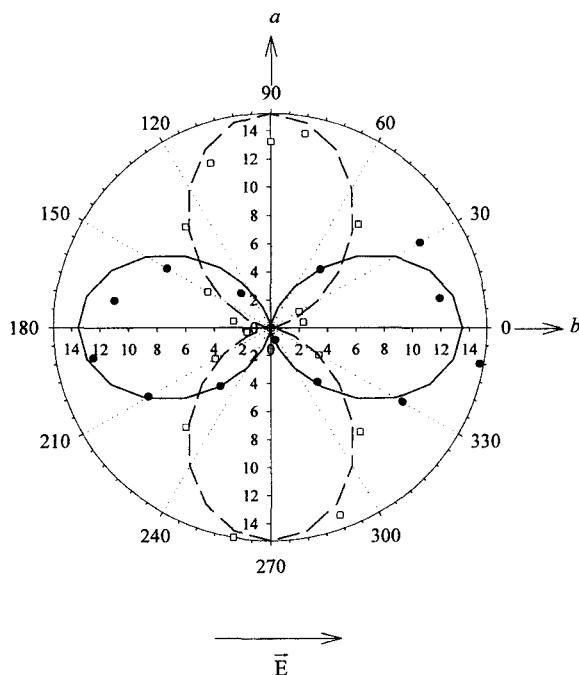


Figure 5. Integrated intensity of the 107- (●) and 110-cm⁻¹ (□) FIR absorption bands of K⁺, as a function of the angle of rotation between \vec{E} and b . The muscovite crystal is rotated about an axis parallel to c^* . — Calculated curve, $I_{\max} = 13.5$; - - Calculated curve, $I_{\max} = 15.25$.

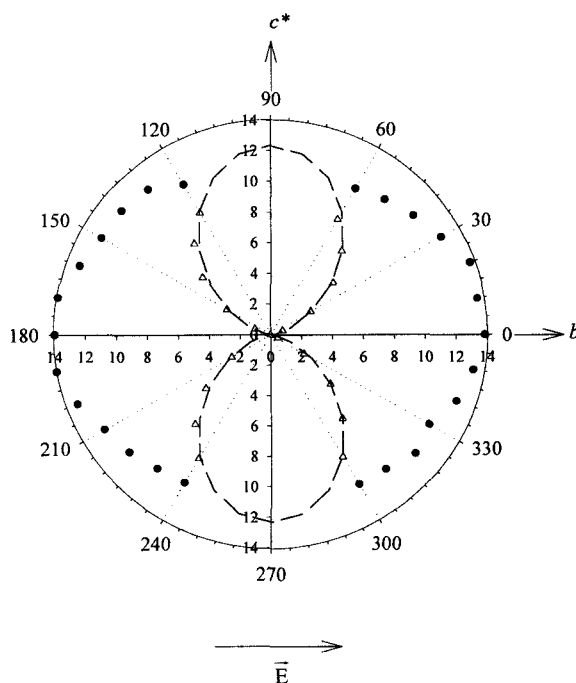


Figure 6. Integrated intensity of the 107- (●) and 143-cm⁻¹ (Δ) FIR absorption bands of K⁺, as a function of the angle of rotation between \vec{E} and b . The muscovite crystal is rotated about the a axis. — Calculated curve, $I_{\max} = 12.33$.

where b , \vec{E} , and $\vec{m}_{107 \text{ band}}$ are parallel. Both components $\vec{m}_{107 \text{ band}}$ and $\vec{m}_{143 \text{ band}}$ are perpendicular (Figure 8b).

Only absorption bands at 110 and 143 cm⁻¹ occur in the (010) plane for rotation about b (Figure 4). The intensities of both bands are plotted *versus* ϕ in Figure 7. The calculated values fit the experimental data well for the 143-cm⁻¹ band, but not for the 110-cm⁻¹ band. Nevertheless, the maximum intensity of the 110-cm⁻¹ band occurs where a , \vec{E} , and $\vec{m}_{110 \text{ band}}$ are parallel. Both components, $\vec{m}_{110 \text{ band}}$ and $\vec{m}_{143 \text{ band}}$, are perpendicular (Figure 8c).

Space group and site symmetry considerations

In the optically active vibrational modes of crystals, all primitive unit cells vibrate in phase over long distances compared with the unit-cell dimensions. Thus, the fundamental crystal vibrations can be assigned to the point-group symmetry equivalent to the space group without translational features. The muscovite structure is conventionally described with a C -centered unit cell ($C1\ 2c\ 1$) which contains two primitive (P) unit cells for which the equivalent point group is C_{2h} . The P cell contains two potassium cations which lie on C_2 axes, parallel to the b axis of the crystal. They are related through a center of symmetry (Fletcher *et al.*, 1996).

Reference to the table for C_{2h} symmetry in Farmer (1974b) shows that the potassium ions contribute one

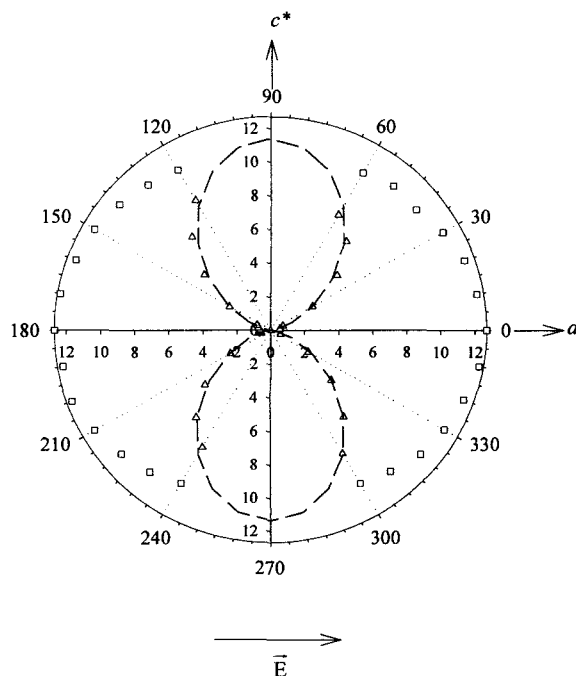
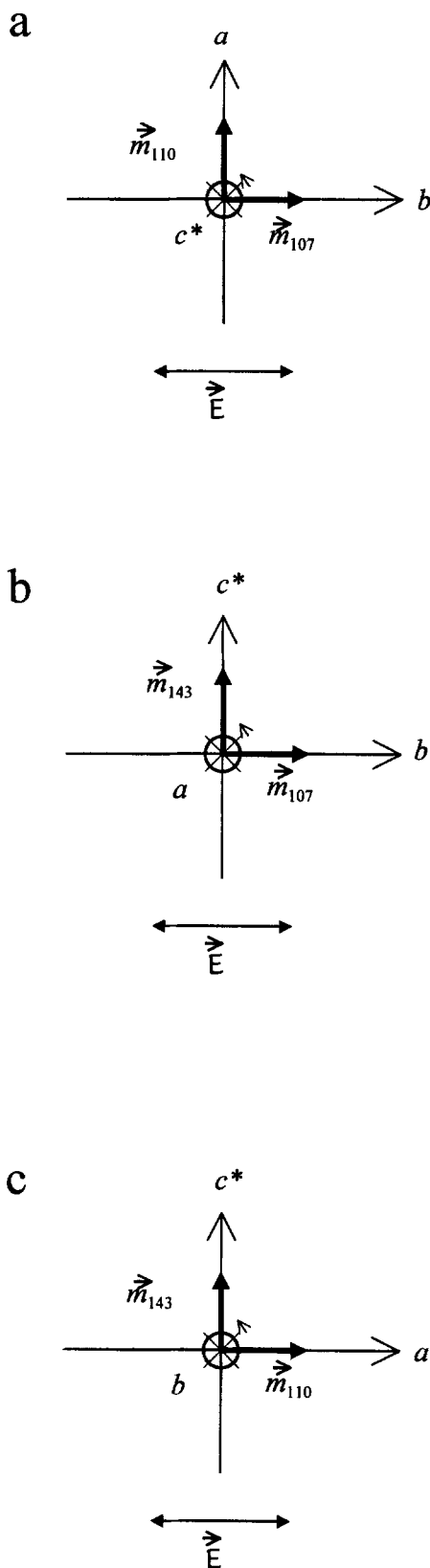


Figure 7. Integrated intensity of the 110- (□) and 143-cm⁻¹ (Δ) FIR absorption bands of K⁺, as a function of the angle of rotation between \vec{E} and a . The muscovite crystal is rotated about the b axis. — Calculated curve, $I_{\max} = 11.37$.



vibration to each of the A_u and A_g symmetry types of the crystal and two vibrations to each of the B_u and B_g symmetry types. The A_u vibration develops a transition moment parallel to b , and the B_u transition moments are perpendicular to b , but their directions in this plane are not specified by the site symmetry. The A_g and B_g vibrations are inactive in the infrared, but potentially active in Raman spectra.

Inspection of the immediate environment of the potassium shows that the coordinating oxygen atoms are approximately related by a C_{3i} axis of symmetry parallel to c^* with the potassium ion on the inversion center. If the symmetry were exact for a C_{3i} axis, then the potassium vibrations would consist of a doubly degenerate vibration perpendicular to c^* and a vibration parallel to c^* . Because the symmetry is only approximate, the degenerate vibration is split to give two in-plane vibrations at 107 and 110 cm^{-1} . The space-group symmetry requires that in the 107- cm^{-1} vibration, the potassium ions vibrate parallel to b , and hence it is an A_u -type vibration. The other vibration, at 110 cm^{-1} , is a B_u type in which the potassium motion is perpendicular to b and thus parallel to a . The 143- cm^{-1} vibration, which is parallel to c^* , is another B_u type. Thus, the observations reported here match exactly the predictions based on the local site symmetry and environment of the potassium.

The out-of-plane potassium vibration at 143 cm^{-1} , which has a much higher frequency than those of the in-plane vibrations, is not indicative of a force constant of this vibration being much larger than those of the in-plane vibrations. For infrared observations using crystal sheets substantially thinner than the exciting radiation, out-of-plane absorption bands are observed at a frequency corresponding to the longitudinal vibrational mode of bulk crystals. Where a strong dipole oscillation is generated by the vibration, this longitudinal frequency is substantially higher than that of the corresponding transverse vibrational mode. The in-plane vibrations of thin sheets are observed at the frequency of the transverse mode (Farmer and Russell, 1966), and this alone may account for the difference in frequency.

The 165- cm^{-1} band shows little or no variation in intensity or frequency as the crystal is rotated around c^* and this suggests that it arises from the vibration of atoms which are related by the approximate C_{3i} symmetry. The 187- cm^{-1} band is clearly an A_u vibration which has no corresponding B_u vibration in the spectrum. Hence, this band is probably associated with the octahedral sheet, which deviates considerably from C_{3i} symmetry.

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Figure 8. Orientation with respect to the crystallographic axes of the vibration modes of K^+ in muscovite.

ACKNOWLEDGMENTS

The authors are grateful to S. Guggenheim for reading and correcting the manuscript.

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(Received 7 April 1999; accepted 6 April 2000; Ms. 331; A.E. William F. Bleam)