

ASSIGNMENT OF THE FAR-INFRARED ABSORPTION BANDS OF K IN MICAS

V. LAPERCHE AND R. PROST

Station de Science du Sol, INRA, Route de Saint-Cyr,
F-78026 Versailles, France

Abstract—To identify the far-infrared (FIR) absorption bands related to K cations in micas, spectra of muscovite, phlogopite, and biotite were compared with the spectra of pyrophyllite and talc, which have no compensating cations, and to the spectra of micas in which K is substituted by mono- and divalent cations. Dichroic experiments using single crystals of these micas showed that some of the bands or components related to K have a strong in-plane and out-of-plane dichroic character. These experimental data led to the assignment of the FIR bands at 110, 91, and 83 cm^{-1} for muscovite, phlogopite, and biotite, respectively, which have no in-plane and out-of-plane dichroic character, to the vibration of the double ring of oxygen atoms that constitutes the cage in which K is located (mode III).

Bands at 146, 136, and 152 cm^{-1} for muscovite, phlogopite, and biotite, respectively, which have a strong out-of-plane dichroic character, were assigned to the out-of-plane vibrations of K atoms (mode IV). Some of the components at 190, 158–153, and 145–124 cm^{-1} for muscovite, phlogopite, and biotite, respectively, which have a strong in-plane dichroic character, are possibly related to the in-plane vibrations of K atoms (modes I and II). The 165- cm^{-1} band of muscovite is a lattice mode of vibration. Frequencies of modes III and IV of the compensating cations of micas in which K was substituted by mono- and divalent cations exchanged as a function of $\sqrt{Z/m}$ where Z is the charge and m the mass of the cation. Modes III and IV were well resolved and very sensitive to the crystallochemical properties of the structure (di- or trioctahedral character, Fe content, etc.). FIR spectroscopy may therefore be an important tool that uses compensating cations as probes to study the interactions between the cations and the structure of mica minerals.

Key Words—Dichroism, Far-infrared spectroscopy, Mica, Potassium, Vermiculite.

INTRODUCTION

Insofar as pedology, agronomy, and environment science are concerned with the dynamics of cations, the physicochemical state and location of compensating cations in the interlamellar spaces of clays and related minerals must be considered. Indeed, the vermiculitization of micas, which was of considerable interest to researchers during the period 1960–1975, cannot be fully understood because of a lack of knowledge concerning the specific interactions at the molecular level between K cations and the structure (Norris, 1972; Robert and Pédro, 1972; Rousseau *et al.*, 1972; Scott *et al.*, 1972; Kodama and Ross, 1972). For the same reasons, the mechanism of K fixation by K-montmorillonite subjected to wetting and drying cycles or by illitization are not completely understood to this day (Eberl *et al.*, 1986; Inoué *et al.*, 1988). In the same way, cation-exchange selectivity, has not yet been fully explained because the identification and characterization of so-called selective sites has not been possible. Heretofore, these phenomena have been studied at the macroscopic level by ion exchange, X-ray powder diffraction (XRD), electron microscopy etc.

Specific reagents used for the selective extraction of cations for quantitative determinations necessarily induce changes in the system, and information on the physicochemical state of cations in the interlamellar

spaces is difficult to deduce from this procedure. In the same way, XRD gives only the mean position of compensating cations, and electron microscopic techniques produce information on the stacking of layers and particles. As a consequence, the nature of the interactions between compensating cations and the structure of clays and their location at a molecular level is still lacking.

To obtain information on the *in situ* state and the location of compensating cations, Prost and Laperche (1990) and Laperche *et al.* (1990) used far-infrared spectroscopy (FIR) and solid-state nuclear magnetic resonance (NMR). Indeed, using the cations themselves as probes, spectroscopic techniques can provide information on the nature of the interactions between compensating cations and the structure of clays which may allow the different fixation sites to be identified and characterized. This point is of considerable significance in understanding the fate of cations, in particular, heavy metals in soils.

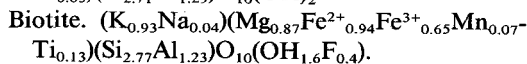
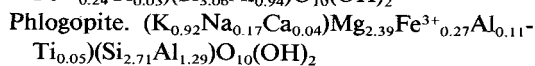
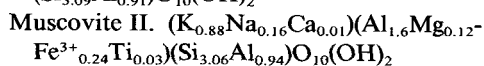
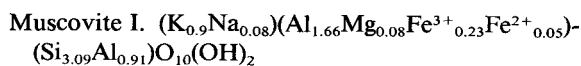
The observed IR absorption bands of micas in the 200–80- cm^{-1} range, were assigned by Ishii *et al.* (1967), using a normal mode analysis, to interlayer and K vibrations. Farmer (1974) assigned bands of micas at about 100 and 150 cm^{-1} to the in-plane and out-of-plane vibrations of K, respectively. Using the Black Jack Mine beidellite and the Llano vermiculite, both saturated with mono- and divalent cations, Fripiat

(1981) identified two sets of bands and assigned them to the in-plane (ν_{\parallel}) and the out-of-plane (ν_{\perp}) vibrations of compensating cations.

In our effort to use the compensating cations themselves as probes to study the clay-cation interactions, more precision was needed concerning the assignment of the absorption bands of phyllosilicates in the far-infrared range (250–30-cm⁻¹). The aims of the present report are to compare the far-infrared spectra of micas to those of pyrophyllite and talc, which have no compensating cations, and to the same micas in which K was replaced by mono- and divalent cations. The experimental data were completed by in-plane and out-of-plane dichroic experiments.

MATERIALS AND METHODS

Muscovite, phlogopite, and biotite from Madagascar, having the following chemical formula were used:



Powders were prepared (<20- μ m fraction for muscovite; <50- μ m fractions for phlogopite and biotite) by grinding the micas under water.

The potassium of the <50- μ m size fraction of phlogopite was extracted with a 2 M sodium nitrate solution heated at 80°C. Complete extraction took one month. The Na-vermiculite obtained was then exchanged with mono- and divalent cations to produce Na-, K-, Rb-, Cs, NH₄-, and Ba-phlogopites ("mica" is used here instead of vermiculite to avoid confusion with samples obtained after K was removed from phlogopite, biotite, and muscovite). Four treatments of 24 hr each at 80°C with a 0.5 M solution of the corresponding chloride salt were needed to obtain a complete exchange. The completeness of exchange was checked with an energy dispersive microanalysis device. The potassium of <20- μ m fraction of muscovite and the <50- μ m fraction of biotite was extracted at 26°C with a solution made of a mixture of 0.2 N Na-tetraphenylboron and 3.8 N NaCl. Complete extraction, checked by XRD took 45 days for muscovite and 7 days for biotite. K-tetraphenylboron crystals were removed from the vermiculite suspension by Stokes law settling in three successive sedimentations. Excess NaCl was removed from the suspension during these sedimentations and self-supporting films were prepared by filtration. The absence of K-tetraphenylboron was checked by XRD and FIR.

To identify bands in the 220–30-cm⁻¹ infrared range due to K, the spectra of pyrophyllite, talc, and substituted micas (muscovite, phlogopite, and biotite in which K was replaced by mono- and divalent cations) were compared. Because the normal mode analysis of layers of micas made by Ishii *et al.* (1967) shows (Figures 8 and 9 of their paper) that each transition moment corresponding to interlayer and K vibrations has a specific orientation with respect to the *a*, *b*, and *c* axis of the crystal, dichroic experiments around the *c* and *a* or *b* axis were performed. Indeed, the intensity of absorption in a crystal is a function of the angle α between the electric field \vec{E} of the polarized radiation and the transition moment \vec{M} , as shown in Eq. (1) (Fripiat *et al.*, 1965):

$$A = \log(I_0/I) = ke \cos^2 \alpha / \cos r, \quad (1)$$

where I_0 is the intensity of the incident beam, I is the intensity of the transmitted beam, k is the extinction coefficient, e is the thickness of the crystal, α is the angle between the vibrational moment \vec{M} and the electric field \vec{E} of the polarized beam, and r is the refraction angle of the beam in the crystal.

Spectra were recorded with a Bruker IFS 113V spectrometer. The spectrometer was operated under vacuum and was equipped with a mercury source, a TGS detector, which was working in the 500–10-cm⁻¹ range, and a mylar beam splitter 12- and 23- μ m thick, which covered the 250–40-cm⁻¹ range. A polarizer (SPECAC) was used that fixed the orientation of the electric field \vec{E} of the IR beam.

FIR spectra were recorded after 100 scans, with a scanning speed of 0.59 mm/s and a resolution of 2 cm⁻¹, for samples prepared in three different ways: (1) pellets were made of a mixture of 10 mg of clay and 30 mg of polyethylene; (2) self-supporting films were prepared by filtering the suspension under vacuum on a Millipore filter. The clay film was separated from the Millipore filter; (3) single crystals of muscovite, phlogopite, and biotite were cut, 2 × 3 cm in size and whose thickness was, respectively, 108, 30, and 75 μ m. The *a* and *b* axis were deduced from a Laue diagram. For the dichroic experiments, spectra were recorded by rotating these single crystals around the *c* axis (in-plane dichroism) (Figure 1a) or around the *b* axis, which was perpendicular to the electric field \vec{E} (out-of-plane dichroism) (Figure 1b). The electric field \vec{E} was kept horizontal.

RESULTS

To identify the absorption bands of K in micas, FIR spectra of muscovite I, phlogopite, and biotite were compared with those of pyrophyllite and talc, which have no compensating cations, and to substituted micas in which K was replaced by mono- and divalent cations. Muscovite I and pyrophyllite are both dioc-

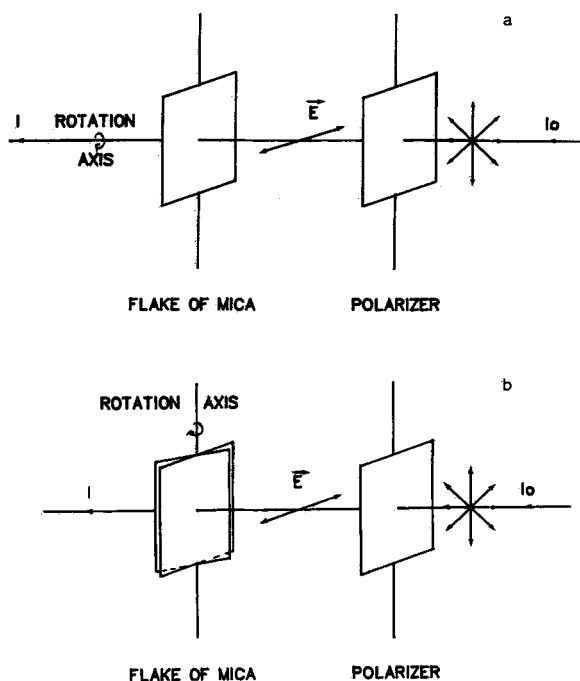


Figure 1. Diagram of the dichroic experiment. (a) Single crystal of mica is rotated around its *c* axis to study the dichroic effect of vibrational moments parallel to the (*a*, *b*) plane of the layer; (b) The single crystal of mica is rotated around its *b* axis to study the dichroic effect of vibrational moments perpendicular to the (*a*, *b*) plane of the layer.

tahedral minerals, whereas phlogopite, biotite and talc are trioctahedral.

FIR spectra of micas, pyrophyllite, and talc

Figure 2 shows the spectra of muscovite I, phlogopite, biotite, pyrophyllite, and talc, all obtained by the polyethylene pellet technique using the same amount of material. The small absorption band marked with an asterisk is due to the 72-cm⁻¹ polyethylene absorption band. Another tiny absorption band can be seen in the spectra of pyrophyllite and talc, respectively, at 112 and 100 cm⁻¹. Its intensity is very weak with respect to the intensity of the low-frequency band of muscovite, phlogopite, and biotite, respectively, at 110, 91, and 83 cm⁻¹.

Pyrophyllite shows bands at 162, 185 and 201 cm⁻¹ (Figure 2, curve 1), which are close to the 167 and 190-cm⁻¹ bands of muscovite I (Figure 2, curve 2). Talc shows two well-resolved bands at 168 and 177 cm⁻¹ (Figure 2, curve 3), whereas the spectra of phlogopite and biotite have bands, respectively, at 156 and 128–139 cm⁻¹ (Figure 2, curves 4 and 5).

FIR spectra of micas and micas containing mono- and divalent cations

To identify the FIR bands which are related to K, spectra of K-micas were compared with spectra of mi-

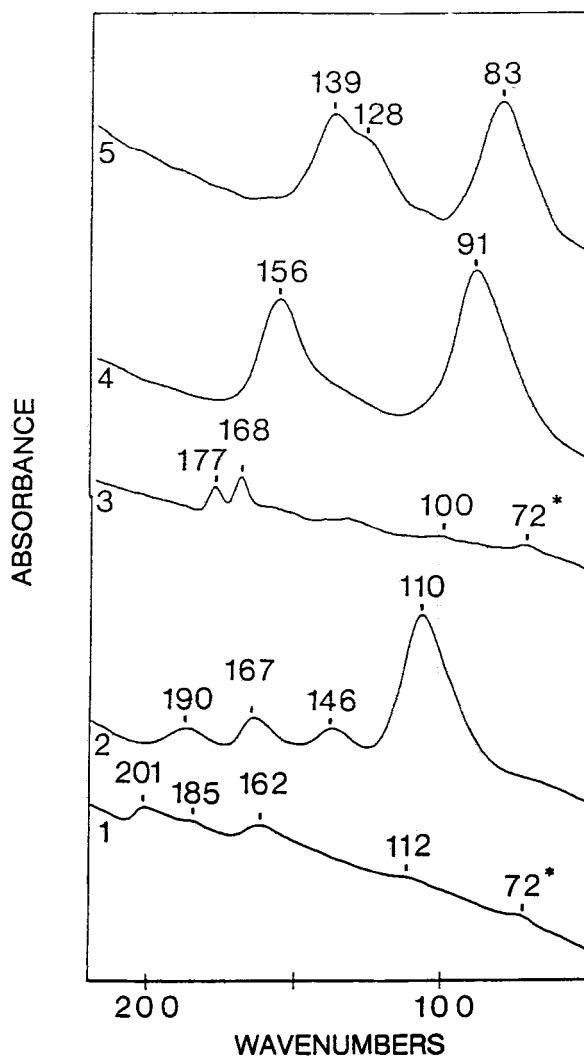


Figure 2. Far-infrared spectra obtained by the polyethylene pellet technique of: (1) pyrophyllite, (2) muscovite I, (3) talc, (4) phlogopite, (5) biotite. Pellets were prepared by mixing 10 mg of clay with 30 mg of polyethylene.

cas in which K had been exchanged by mono- and divalent cations. Figure 3a shows spectra of self-supporting films of Na-, NH₄-, Rb-, K-, Cs-, and Ba-phlogopite. Small shifts and changes in the profile of the 156-cm⁻¹ band can be noted for samples in which K was exchanged by mono- and divalent cations. These changes are probably due to several reasons, one of them being related to the nature of the compensating cations. The 91-cm⁻¹ absorption band is absent in the spectra of Na- and Ba-phlogopite (Figure 3a, curves 2 and 6) which are homoionic samples, but it is present with a lower intensity in the spectra of NH₄-, Rb-, and Cs-phlogopite in which K was not completely removed. Two new absorption bands at 105 and 72 cm⁻¹ can be seen for Ba-phlogopite; but only a single new,

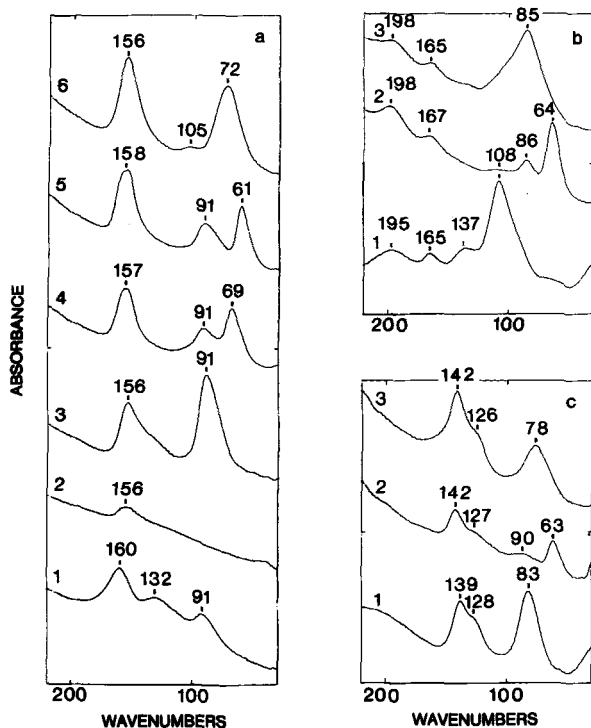


Figure 3. Far-infrared spectra of micas in which K was replaced by mono- and divalent cations. (a) phlogopite, 1 = NH_4^+ , 2 = Na, 3 = K, 4 = Rb, 5 = Cs, 6 = Ba; (b) muscovite, 1 = K, 2 = Cs, 3 = Ba; (c) biotite, 1 = K, 2 = Cs, 3 = Ba.

well-resolved band is present at 132, 72, 69, and 61 cm^{-1} for NH_4^+ , Ba-, Rb-, and Cs-phlogopite, respectively. The absence of the 91- cm^{-1} band in the spectra of Na- and Ba-phlogopite, the decrease in intensity of this band in the spectra of NH_4^+ , Rb-, and Cs-phlogopite, and the existence of new bands if K was replaced by mono- and divalent cations suggest that the 91- cm^{-1} band is related to K. One component of the 156- cm^{-1} band is also related to K.

Figure 3b shows spectra obtained on self-supporting films of muscovite II, in which K was replaced by Cs and Ba. The intensity of the 108- cm^{-1} band is very weak, and new bands are present at 86 and 64 cm^{-1} for Cs-muscovite II and at 85 cm^{-1} for Ba-muscovite II. The 165- cm^{-1} band did not shift if K was replaced by Cs or Ba. The 195- cm^{-1} band was only weakly affected if K was replaced by Cs or Ba. Thus the 108- cm^{-1} band and one component of the 195- cm^{-1} band appear to be related to K located in the interlamellar spaces of muscovite.

Figure 3c shows spectra of self-supporting films of biotite in which K was completely replaced by Cs and Ba. As it was noted for phlogopite, the high-frequency component at 139 cm^{-1} was weakly affected by the exchange, but the 83- cm^{-1} band was absent and new bands were present at 78 cm^{-1} for Ba-biotite and at

63 and 90 cm^{-1} for Cs-biotite. Thus, the 83- cm^{-1} band and one component of the 139- cm^{-1} band appear to be related to K in the interlamellar spaces of biotite.

Dichroic experiments

To check the existence in the FIR spectra of micas of modes of vibration that have a dichroic character, dichroic experiments were performed on single crystals of muscovite I, phlogopite, and biotite. The experiments were performed in-plane (a) and out-of-plane (b). To obtain an in-plane dichroic effect, the crystal had to be rotated around its c axis (Figure 1a). The lowest frequency absorption bands of muscovite I (Figure 4b), biotite (Figure 4d), and phlogopite (Figure 4f) at 110, 83, and 91 cm^{-1} , respectively, had no in-plane dichroic character. Spectrum 1 corresponds to the orientation of the single crystal in which the a axis was parallel to the electric field \vec{E} of the polarized electromagnetic wave (Figure 1a).

Muscovite I had two bands at 167 and 190–195 cm^{-1} (Figure 4a). The 167- cm^{-1} band, which was not affected by the exchange of K by Cs or Ba, had no dichroic character. Only the 190- cm^{-1} band displayed a dichroic character when the sample was rotated around the c axis. The intensity of the 190- cm^{-1} component increased and then decreased as a function of the angle of rotation, α . Maximum absorption occurred when the a axis was perpendicular to \vec{E} , but it was never equal to zero. Hence, the 190- cm^{-1} band received contributions from at least two components, one of which corresponds to a transition moment whose projection on the (a, b) plane is parallel to the b axis. This experiment could not determine the dichroic character of the other component.

Figure 4c shows the presence of two bands at 124 and 145 cm^{-1} for biotite. These bands had a strong dichroic character when the sample was rotated around the c axis. The intensity of the 124- cm^{-1} component became equal to zero if $\alpha = 0$. Consequently, the corresponding transition moment was parallel to the b axis. The 145- cm^{-1} band had its transition moment perpendicular to the first one. The intensity of the 145- cm^{-1} component was never equal to zero, possibly because of the presence of a third component.

Figure 4e shows the presence of a single band at 153–158 cm^{-1} for phlogopite. Changes observed if the single crystal was rotated around the c axis suggest that this band was made of at least two components whose transition moments were perpendicular. According to the calculations of Luck and Ditter (1967–68), the overlap of components at 153–158 cm^{-1} ($\Delta\nu_{\text{max}} = 5 \text{ cm}^{-1}$), whose halfwidth $\Delta\nu_{1/2} = 12 \text{ cm}^{-1}$, give only one band. Phlogopite had the same dichroic character as biotite, but the corresponding components were not resolved. To obtain an out-of-plane dichroic effect, the crystal had to be rotated around the a or the b axis (Figure 1b). The low-frequency band at 110, 91 and 83 cm^{-1}

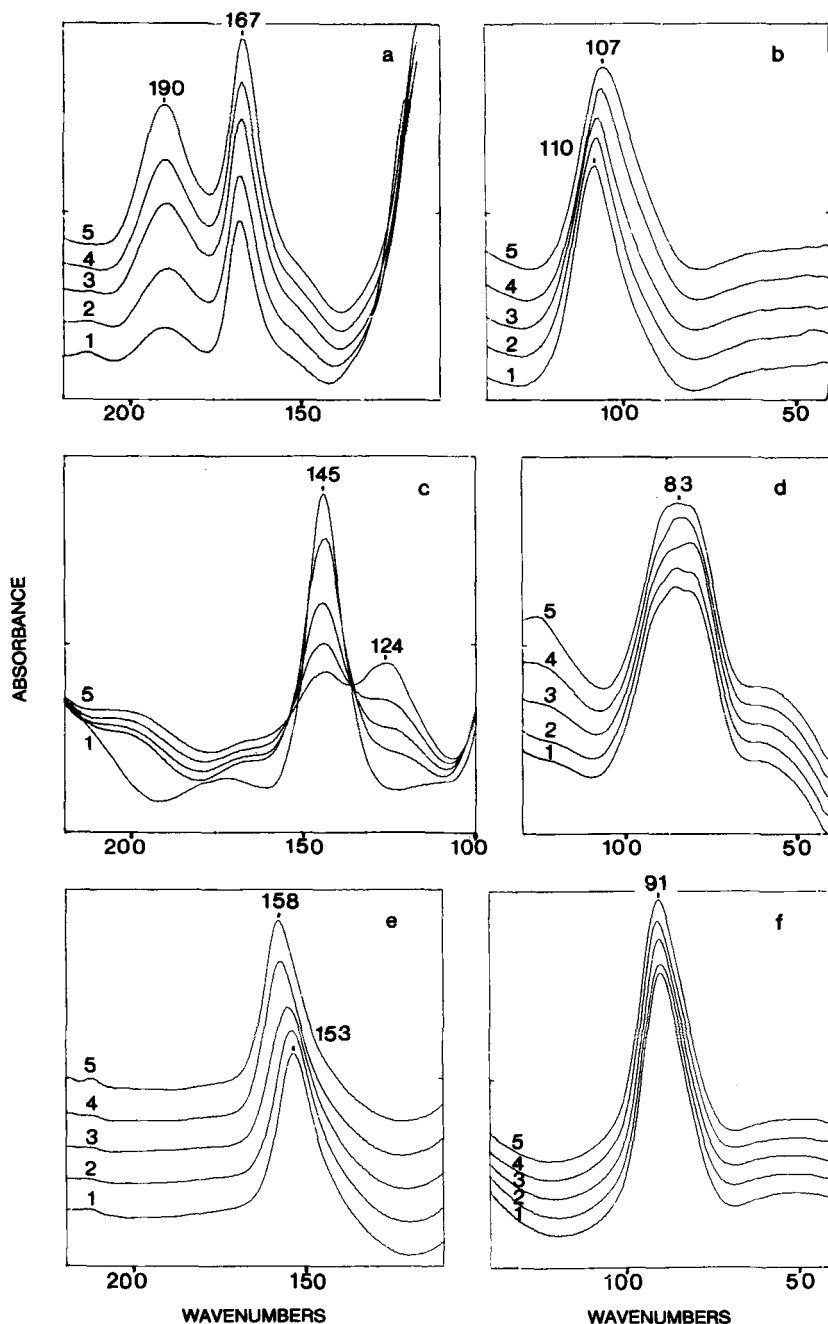


Figure 4. In-plane dichroic effect of far-infrared absorption bands of single crystals of: (a and b) muscovite; (c and d) biotite; (e and f) phlogopite. Spectra were obtained as a function of the rotation angle, α , between a axis and electric field \vec{E} in the (a , b) plane. (1) $\alpha = 0^\circ$; (2) $\alpha = 20^\circ$; (3) $\alpha = 40^\circ$; (4) $\alpha = 70^\circ$; (5) $\alpha = 90^\circ$.

for muscovite I, phlogopite, and biotite, respectively, had no dichroic character if the single crystal was rotated around the a or the b axis. Only the higher frequency components were discussed by those authors. Figures 5a, 5b, and 5c show the IR spectra of single crystals of muscovite I, biotite, and phlogopite, respectively, that were tilted around the b axis (the a axis

was parallel to \vec{E}). A band having a strong out-of-plane dichroic character was noticed at 146, 136, and 152 cm^{-1} for muscovite I, biotite, and phlogopite.

DISCUSSION

Comparison of the FIR spectra of muscovite, phlogopite, and biotite to the spectra of pyrophyllite and

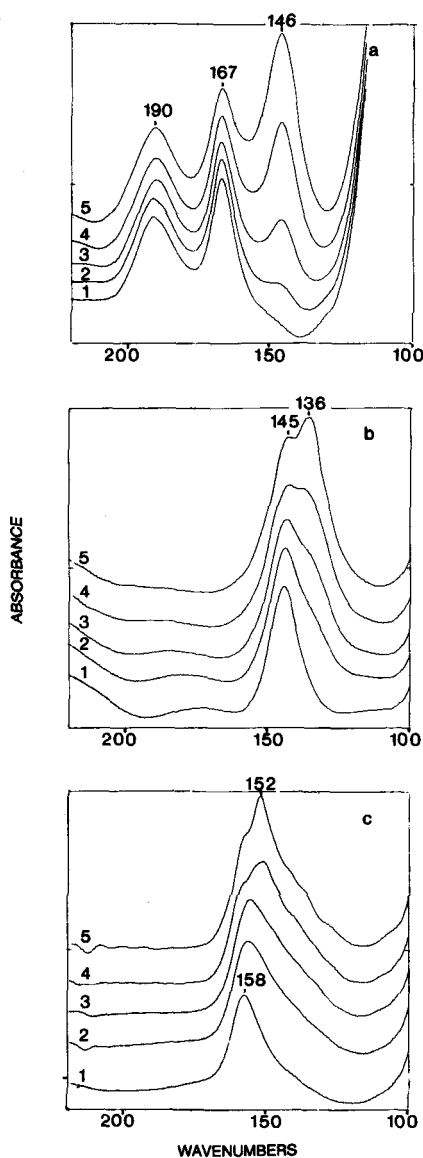


Figure 5. Out-of-plane dichroic effect of far-infrared absorption bands of single crystals of (a) muscovite; (b) biotite; (c) phlogopite. Spectra were obtained as a function of rotation angle, α , between c axis and electric field \vec{E} : (a) muscovite: (1) $\alpha = 90^\circ$, (2) $\alpha = 80^\circ$, (3) $\alpha = 70^\circ$, (4) $\alpha = 60^\circ$, (5) $\alpha = 50^\circ$; (b) biotite: (1) $\alpha = 90^\circ$, (2) $\alpha = 50^\circ$, (3) $\alpha = 40^\circ$, (4) $\alpha = 35^\circ$, (5) $\alpha = 33^\circ$; (c) phlogopite: (1) $\alpha = 90^\circ$, (2) $\alpha = 60^\circ$, (3) $\alpha = 50^\circ$, (4) $\alpha = 40^\circ$, (5) $\alpha = 35^\circ$. The single crystal was rotated around its b axis.

talc, which have no compensating cations, and to the spectra of micas in which K was substituted by mono- and divalent cations, shows clearly the presence of absorption bands that are more or less affected by compensating cations. The low-frequency band at 110, 91, and 83 cm^{-1} for muscovite, phlogopite, and biotite, respectively, does not exist in pyrophyllite and talc, and it shifts to higher or lower frequencies as a function

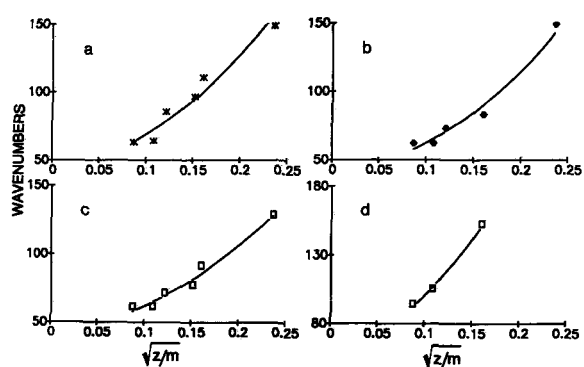


Figure 6. Plots of the low-frequency absorption band of compensating cations of micas in which K was replaced by mono- and divalent cations as a function of $\sqrt{Z/m}$. (a) muscovite (mode III), (b) biotite (mode III), (c) phlogopite (mode III), (d) phlogopite (mode IV).

of the mass of the cations that replace K in the micas. Fripiat (1981) found for the Llano vermiculite a relationship between the frequency of the low-frequency band and the square root of the charge, Z , divided by the mass m of compensating cations. Data in Table 1 plotted on Figures 6a, 6b, and 6c, which correspond respectively to muscovite II, biotite, and phlogopite in which K was replaced by mono- and divalent cations, give non-linear relationships between the frequency ν and $\sqrt{Z/m}$ similar to those obtained for the Llano vermiculite saturated by NH_4 , K, Sr, Cd, Ba, Rb, and Cs (unpublished data from this laboratory). Thus, the low-frequency band at 110, 91 and 83 cm^{-1} for muscovite, phlogopite, and biotite, respectively, is assigned to a mode of vibration in which the contribution of K is important. This band was used to study K in micas (Prost and Laperche, 1990). A similar relationship (Figure 6d) was found for the frequency of the 152- cm^{-1} band of phlogopite, which has an out-of-plane dichroic character, indicating that this band is also related to a mode of vibration in which K is involved. The greater change in frequency of the out-of-plane dichroic band compared with the low-frequency mode (Figure 6) shows that the contribution of the compensating cations to the out-of-plane mode of vibration was greater than for the preceding one. Fripiat (1981) noted the same behavior for the ν_{\parallel} and ν_{\perp} modes of vibration of compensating cations in the Llano vermiculite. Hence, bands at 146, 136 and 152 cm^{-1} for muscovite I, biotite, and phlogopite, respectively, which are affected by the substitution of K by mono- and divalent cations, are assigned to a mode of vibration in which the contribution of K is important.

The substitution of K in micas by mono- and divalent cations (Figure 3) shows that the 156, 139–128, and 195- cm^{-1} band of phlogopite, biotite, and muscovite, respectively, have at least one component corresponding to mode of vibration in which K is involved. The small frequency shifts observed as a

function of $\sqrt{Z/m}$ show that the contribution of compensating cations to this mode of vibration is weak. The 165–167-cm⁻¹ band of muscovite and some components at 156, 139–128, and 195 cm⁻¹ for phlogopite, biotite and muscovite, respectively, were not affected by the exchange of K by mono- and divalent cations (Figure 3). These absorption bands are related to lattice vibrations in which compensating cations have no effect. The 165–167-cm⁻¹ band of muscovite, a dioctahedral mineral, is also close to the 162-cm⁻¹ band of pyrophyllite (Figure 2), which is also dioctahedral, but which lacks compensating cations. Two bands at 201 and 185 cm⁻¹ were also observed for pyrophyllite at frequencies close to the 190–195-cm⁻¹ components of muscovite, which do not shift if K is substituted by mono- and divalent cations. These bands or components are also assigned to lattice vibrations that are not affected by compensating cations. The FIR spectra of trioctahedral minerals were different from spectra of dioctahedral minerals. Only a doublet at 168–177 cm⁻¹ was observed for talc (Figure 2, curve 3), which possibly corresponds to the components of bands at 156 and 139–128 cm⁻¹, which were not affected by the substitution of K by mono- and divalent cations.

According to Ishii *et al.* (1967), the shift of some components to lower frequencies, with respect to the 168–177-cm⁻¹ bands observed for talc, is possibly due to the substitution in the octahedral sheet of Mg by an increasing amount of Fe in phlogopite and biotite. Indeed, for annite, a trioctahedral mineral containing only Fe in the octahedral sheet, the following shifts have been observed: 168–177 cm⁻¹ for talc, 156 cm⁻¹ for phlogopite, 139–128 cm⁻¹ for biotite, and 133–123 cm⁻¹ for annite. The intensity of the 168–177-cm⁻¹ band of talc is much weaker than the intensities of the observed bands at 158–153 and 145–124 cm⁻¹ for phlogopite and biotite, respectively. The intensity of the 156-cm⁻¹ band of phlogopite in which K was substituted by Na is much lower (Figure 3a, curve 2) compared with the intensity of the 156-cm⁻¹ band of phlogopite (Figure 3a, curve 3), which corresponds to the same amount of material. Here, no absorption band due to Na was observed, indicating that the 156-cm⁻¹ band was, as was discussed above, with respect to the small shifts and changes in the profile of the 156-cm⁻¹ band of phlogopite substituted by mono- and divalent cations (Figure 3), made of several components. Some of these components are apparently related to lattice modes of vibration and some to modes of vibration in which K is involved.

The low-frequency band at 110, 91, and 83 cm⁻¹ for muscovite, phlogopite, and biotite, respectively, due to a mode of vibration in which the contribution of K is important, had no in-plane and out-of-plane dichroic character. Bands at 146, 152, and 136 cm⁻¹ for muscovite, phlogopite, and biotite, respectively, which correspond to vibrations in which the contribution of K

Table 1. Absorption frequencies of mode III and IV of mono- and divalent cations substituted for K of micas.

Mica	Cation				
	K	Rb	Cs	NH ₄	Ba
Muscovite (mode III)	110	64	63	148	85
Biotite (mode III)	83	62	62	149	73
Phlogopite (mode III)	91	61	61	128	71
Phlogopite (mode IV)	152	104	94		

is also important, had a strong out-of-plane dichroic character (Figure 5). The 165–167-cm⁻¹ band of muscovite assigned to a lattice mode of vibration had no in-plane or out-of-plane dichroic character. Bands at 190–195, 156, and 139–128 cm⁻¹ for muscovite, phlogopite, and biotite, respectively, had, for each mineral, components having a strong in-plane dichroic character (Figure 4).

Experimental data reported here allow the assignment of some absorption bands observed in the FIR range of micas, in particular bands corresponding to modes of vibration in which K is involved. Ishii *et al.* (1967) attempted to assign the FIR bands of micas on the basis of the frequency calculations. The question is now to see how the present experimental data support their assignment.

Ishii *et al.* (1967) considered for the FIR absorption range of micas interlayer vibrations whose modes A_u and B_u were presented in their Figure 9 and modes of vibration of K atom between the silicate layers (Figure 7). The A_u and B_u modes of vibration do not include compensating cations, and for dioctahedral minerals, are possibly related to the 162 and 185–201-cm⁻¹ bands of pyrophyllite and to the 165–167 and 190–195 cm⁻¹ components of muscovite, which are not affected by the nature of compensating cations. If the B_u mode of interlayer vibrations is related to the lowest absorption band at 165–167 cm⁻¹ observed for muscovite, this mode has no in-plane dichroic character. For trioctahedral minerals, the A_u and B_u modes are possibly related to the bands at 168 and 177 cm⁻¹ of talc and to the components of the bands at 156 and 139–128 cm⁻¹, respectively, for phlogopite and biotite, which are not affected by the substitution of K by mono- and divalent cations.

The unit cell chosen for the normal mode analysis of K between the layers (Figure 7) comprised only oxygen atoms of the double ring, which forms the cage in which K is located in micas. Experimental data of Prost and Laperche (1990), however, show that the crystallochemical composition of the structure (the di- or trioctahedral character, the Fe content, etc.) has an effect on the vibration frequency of K. They also show that the approximation made by Ishii *et al.* (1967) for their calculations was important and may explain differences between the calculated and the observed absorption frequencies. Modes of vibration I, II, and IV

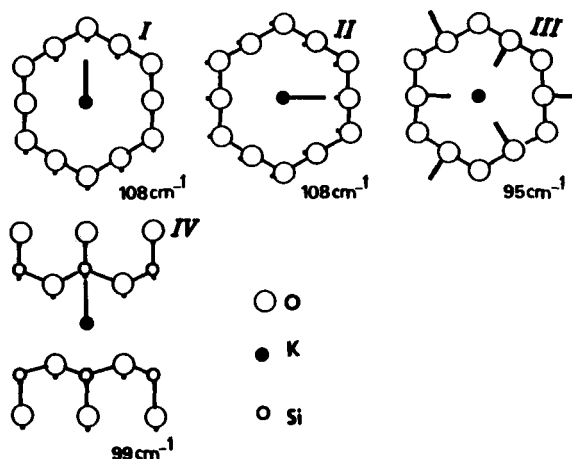


Figure 7. Normal modes of vibration of K in an idealized muscovite according to Ishii *et al.* (1967).

of K between the silicate layers described by Ishii *et al.* (1967) (Figure 7) have transition moments with a given orientation with respect to the crystallographic axis of the mineral. The corresponding absorption bands should have a dichroic character. The transition moment of mode III, which corresponds to the deformation of the double ring of oxygen atoms with respect to K located inside, has no particular orientation with respect to the crystallographic axis.

The dichroic effects observed for bands assigned to modes of vibration in which K is involved suggest the following assignment. Bands at 110, 91 and 83 cm^{-1} for muscovite, phlogopite, and biotite, respectively, which had no in-plane or out-of-plane dichroic character, are assigned to mode III described by Ishii *et al.* (1967). Bands at 146, 136, and 152 cm^{-1} for muscovite, biotite, and phlogopite, respectively, which have a strong out-of-plane dichroic character, are assigned to mode IV described by Ishii *et al.* (1967). These two sets of bands, which correspond respectively to mode III and mode IV, were designed by Farmer (1974) and Fripiat (1981) as the in-plane and out-of-plane vibrations of K in micas. Bands at 190, 158–153 and 145–124 cm^{-1} for muscovite, phlogopite, and biotite, respectively, which have strong in-plane dichroic character, are possibly related to modes I and II described by Ishii *et al.* (1967). Indeed, changes in the frequency and the profile of these bands were observed if K was substituted by mono- and divalent cations, and the dichroic experiments show that the in-plane transition moments corresponding to these bands were perpendicular to each other (Figures 4c and 4e), in good agreement with the orientation of the transition moment of modes I and II.

SUMMARY AND CONCLUSIONS

The experimental approach developed, coupled with the normal mode analysis of Ishii *et al.* (1967), leads

to the identification and aids in the assignment of FIR absorption bands of micas. Bands at 110, 91, and 83 cm^{-1} for muscovite, phlogopite, and biotite, respectively, were assigned to mode III described by Ishii *et al.* (1967). This band has no in-plane or out-of-plane dichroic character; it seems to be very sensitive to the crystallochemical composition of the layers. According to our data, the in-plane modes of vibration of K, modes I and II described by Ishii *et al.* (1967), gave bands at higher frequencies. More work is needed, however, to identify and assign all the bands and components observed in the 190-, 145–124-, and 158–153- cm^{-1} range of muscovite, biotite and phlogopite, respectively. In particular, it is important now to re-determine whether or not the in-plane dichroic bands observed are actually due to vibrations in which K between the layers is weakly involved and which correspond to modes I and II described by Ishii *et al.* (1967). Indeed, the assignment presented here concerning the in-plane dichroic modes of vibration is only supported by the fact that the 165–167- cm^{-1} band of muscovite, which was assigned to a lattice mode of vibration, has no in-plane dichroic character and that the transition moments corresponding to the in-plane dichroic components are perpendicular, which is in good agreement with the normal modes I and II described by Ishii *et al.* (1967). Bands at 146, 136 and 152 cm^{-1} for muscovite, biotite, and phlogopite, respectively, have a strong out-of-plane dichroic character and are assigned to mode IV described by Ishii *et al.* (1967). The frequency of this band is strongly dependent on the nature of the compensating cations.

The high sensitivity of modes III and IV to the nature of compensating cations and to the crystallochemical properties of the structure suggests that FIR can be an important tool to study the interactions between cations and the structure of silicates.

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