THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER-OCTOBER, 1970

THE VIBRATIONAL SPECTRA OF LEAD APATITES[1]

S. R. LEVITT[2] AND R. A. CONDRATE, SR., *Department of Ceramic Science, State University of New York College of Ceramics at Alfred University, Alfred, New York 14802.*

ABSTRACT

The infrared (4000–33 cm^{-1}) and laser-Raman spectra are obtained for the mineralogical lead apatites: pyromorphite $Pb_{10}(PO_4)_6Cl_2$, mimetite $Pb_{10}(AsO_4)_6Cl_2$, and vanadinite $Pb_{10}(VO_4)_6Cl_2$. The lack of Raman spectra has previously led to incorrect interpretation of the spectral data. The ν_2 bending modes of XO_4^{3-} groups are assigned to high frequency, low intensity bands in the infrared spectra. For example, the ν_2-mode for the phosphate ion in pyromorphite occurs at 436 cm^{-1}. Also, simple site group theory is now shown to be inadequate for explaining the vibrational spectra of lead apatites. Factor group analysis based on unit-cell symmetry considerations must be introduced to interpret the vibrational spectra. Finally $\nu_1-\nu_3$ frequency inversion in Raman spectra is noted for both mimetite and vanadinite.

INTRODUCTION

Early investigations of the vibrational spectra of lead apatites (Adler, 1964, 1968) have been limited to the middle infrared spectra (4000–300 cm^{-2}). Recent studies of the laser Raman spectra and infrared spectra including the far infrared region for the calcium apatites have shown that analysis of only middle infrared spectra can lead to incorrect interpretation of the spectral data (Kravitz et. al., 1968; Levitt and Condrate, 1969). In this investigation, we have obtained the infrared spectra (4000–33 cm^{-1}) and the laser Raman spectra of pyromorphite [$Pb_{10}(PO_4)_6Cl_2$], mimetite [$Pb(AsO_4)_6Cl_2$] and vanadinite [$Pb_{10}(VO_4)_6Cl_2$]. Analysis of this data has lead to the assignment of the ν_2 bending modes of the XO_4^{3-}-groups. Also, previous band assignments and spectral interpretations based on site-group analysis are now shown to be invalid. Intermolecular coupling interactions occur in the crystalline lattice and factor-group analyses are necessary to account for the vibrational spectra observed.

EXPERIMENTAL

Materials. Geological pyromorphite from Ems, Germany,[3] mimetite from Tsumeb, South-

---

[1] Presented in part at the 23rd Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, September, 1968, and at the 10th European Congress on Molecular Spectroscopy, University of Liege, Belgium, September, 1969. Submitted by S.R.L. to the Faculty of the College of Ceramics at Alfred University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Present address: Ferro Corporation, Technical Center, 4150 East 56th Street, Cleveland, Ohio 44105.

[3] U. S. National Museum, Cat. No. 104407.

west Africa[1] and vanadinite from San Carlos, Mexico[2] were used in the present investigation. Wet chemical and emission spectrographic analyses confirm the identity of the major constituents and demonstrate the presence of several impurity elements of low concentration, as expected for geologically formed solids. X-ray diffraction patterns were characteristic for the three apatites and indicated a high degree of crystallinity.

Middle-Infrared Spectra. The alkali halide disk technique was employed, using approximately 2 mg of apatite powder in 300 mg of powdered spectroscopic-grade KBr (Harshaw Co.) which had been dried at 110°C and allowed to cool in a vacuum desicator to avoid absorption of moisture. The middle-infrared spectra (4000–400 cm^{-1}) were obtained with a Perkin-Elmer Model 621 double-beam spectrophotometer which was purged free of water vapor and carbon dioxide by a Perkin-Elmer air dryer purging device. The absorption bands of water vapor, carbon dioxide and polystyrene film were used to calibrate the spectra in this region. The wave-number accuracy of all sharp bands was ± 2 cm^{-1}. Spectra of Nujol mulls demonstrated no significant differences with respect to those obtained using KBr pellets.

Far-Infrared Spectra. The far-infrared spectra (800–33 cm^{-1}) were obtained with Nujol mulls on polyethylene film using a Beckman IR-11 double beam grating spectrophotometer. Calibration was carried out using the absorption bands of ammonia gas and polyethylene film. The wave-number accuracy of all sharp bands was ± 2 cm^{-1}. The spectrophotometer was purged with dry air to eliminate moisture. Heavy vertical lines on the spectra indicate regions of differing wave-number scale.

Raman Spectra. Apatite powder was placed in a special Cary sample holder which allowed 180° scattering to be observed. The spectra were obtained using a Cary 81 Raman spectrophotometer with a He-Ne gas laser source. The Stokes spectra were recorded as frequency shifts from the 6328 Å line at room temperature and plotted as wave-number (cm^{-1}) vs. intensity. Calibration was carried out using the spectral bands of CCl_4 and C_6H_6. Wave-number accuracy was ± 2 cm^{-1} for all sharp bands.

RESULTS AND DISCUSSION

Site-Group and Factor-Group Models for Lead Apatites. The space-group of pyromorphite, mimetite and vanadinite is C^2_{6h}-$P6_3/m$ and there are six XO_4^{3-} ions per unit cell (Hendricks *et al.*, 1932; Trotter and Barnes, 1958). The possible site symmetries for this space-group are given as

$$3C_{3h}(2),\ C_{3i}(2),\ 2C_3(4),\ C_i(6),\ C_s(6)$$

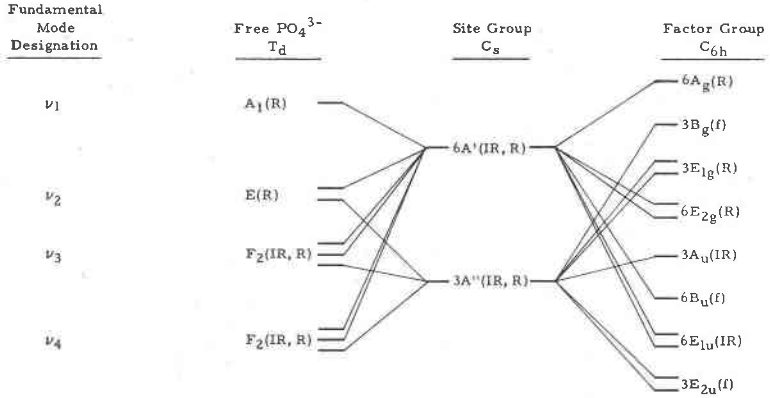
where the point-group is preceded by the number of sets of this kind of site, and is followed in parenthesis by the number of equivalent sites per set. The only set of sites which is completely occupied by six molecules and at the same time is a sub-group of the molecular point-group T_d is a set of C_s sites. Table 1 illustrates the correlation of the XO_4^{3-} fundamentals of the free-ion model (T_d-symmetry) and the site-group model (C_s-symmetry) for pyromorphite, mimetite and vanadinite. For the

---

[1] SUNY, College of Ceramics at Alfred University, Alfred, New York.

[2] Ward's Natural Science Establishment, Rochester, New York.

TABLE 1. CORRELATION CHART FOR XO_4^{3-} FUNDAMENTALS UNDER FREE-ION, SITE—GROUP AND FACTOR—GROUP ANALYSES IN PYROMORPHITE, MIMETITE AND VANADINITE



latter model, all degeneracies are removed, and nine bands should appear coincidently in both the infrared and Raman spectra.

One important fact is neglected by using the site-group method for the interpretation of the vibrational spectra of solids. Strong coupling of vibrational modes of similar molecular groups in a unit cell can occur and alter their vibrational spectra. Similarly to the calcium apatities, the six XO_4^{3-} ions in the unit cell of the lead apatite lattices should interact and couple their vibrational modes. These interactions can be taken into consideration by factor-group analysis using the method proposed by Winston and Halford (1949). The factor-group isomorphous with the space-group C^2_{6h}-$P6_3/m$ is C_{6h}. Factor-group analysis predicts that the nine internal modes split-up into fifty-four crystal modes. From Table 1, we expect nine bands active in the infrared spectra and fifteen bands active in the Raman spectra if there are strong coupling interactions between the XO_4^{3-} ions in the unit cell. Another important result is that none of the frequencies of the vibrational bands in infrared spectra should coincide with those in the Raman spectra and vice versa; except for accidental coincidence which may arise when the splitting between factor-group bands is small.

Interpretation of the Infrared and Laser-Raman Spectra of Pyromorphite. The middle-and-far-infrared spectra of pyromorphite, mimetite and vanadinite are shown in Figure 1 and Figure 2, respectively. The frequencies and qualitative intensities are tabulated in Table 2. Anticipating that factor-group effects exist for these compounds similar to those of the calcium apatites, the band assignments will be discussed accordingly.

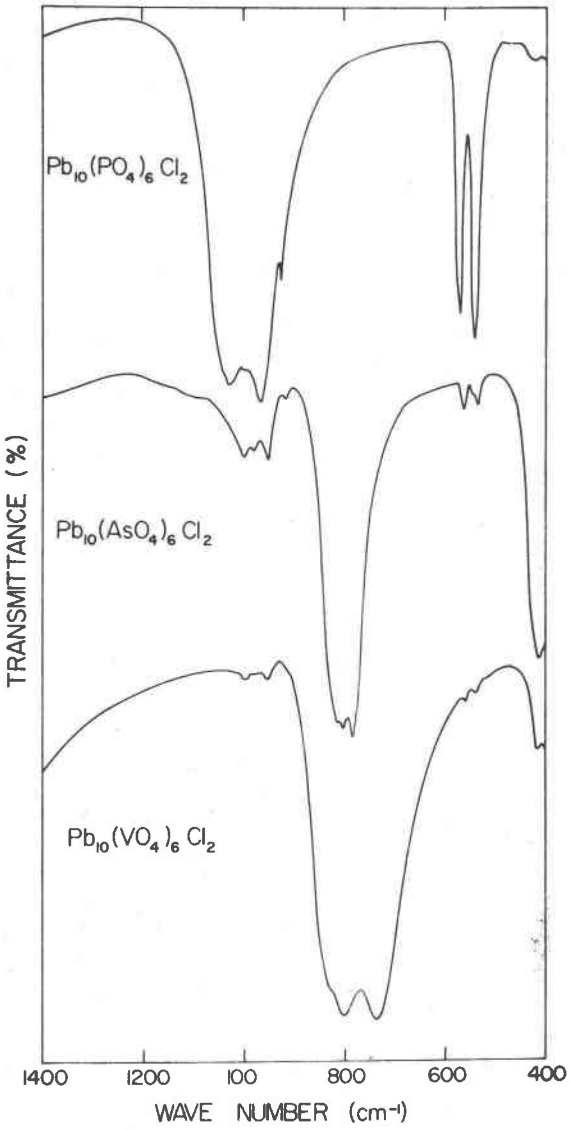


FIG. 1. Middle infrared transmission spectra of pyromorphite, mimetite and vanadinite using the KBr pellet technique.

The middle-infrared spectrum of pyromorphite appears quite similar to that of the calcium apatites. The band assignments of the fundamentals are given in Table 3. In contrast to earlier investigations, the low intensity band at about 436 cm^{-1} is associated with ν_2. The ν_2 mode for

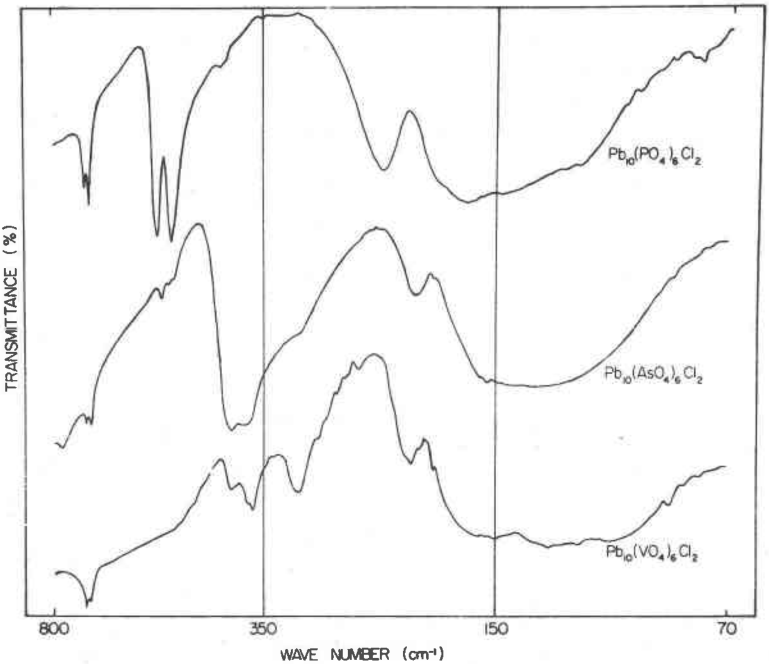


FIG. 2. The far infrared transmission spectra of pyromorphite, mimetite and vanadinite using the Nujol mull technique.

TABLE 2. INFRARED BANDS (CM^{-1}) AND QUALITATIVE INTENSITIES FOR PYROMORPHITE, MIMETITE AND VANADINITE

Pyromorphite	Mimetite	Vanadinite
1031 (vs)	999 (w)	998 (vw)
999 (vs sh)	980 (w)	980 (vw)
967 (vs)	952 (w)	952 (vw)
927 (s sh)	916 (vw)	830 (vs sh)
575 (vs sh)	814 (vs)	801 (vs)
543 (vs sh)	804 (vs)	737 (vs)
436 (vw)	782 (vs)	558 (vw)
245 (s)	560 (vw)	536 (vw)
171 (s b)	545 (vw sh)	419 (m)
148 (s b)	535 (vw)	383 (m sh)
	419 (vs)	374 (m)
	385 (vs)	319 (m)
	319 (m b)	222 (m)
	217 (w b)	150 (s b)
	134 (s b)	132 (s b)

vs—very strong, s—strong, m—medium, w-weak, vw—very weak, sh—sharp, b—broad.

TABLE 3. BAND ASSIGNMENTS (cm^{-1}) FOR THE PO_4^{3-} GROUP IN PYROMORPHITE

	PO_4^{3-}	Adler Infrared	Present Work	
			Infrared	Raman
ν_1	940	926	927	920
ν_2	420		436	413
				394
ν_3	1020	1022	1031	1014
		967	999	980
			967	947
ν_4	560		575	577
			543	552
				541

the fluorapatite appears in the same region of the spectra (Levitt and Condrate, 1969). This band appears to be split into two components but the spectrum is poorly resolved. This splitting is expected for the originally doubly-degenerate ν_2 mode. Also, its low intensity is expected for a band which has become active due to distortion of PO_4^{3-} from T_d symmetry. The remaining far-infrared spectrum is poorly defined, the two predominant features being a strong band at 245 cm^{-1} and a very broad region of absorption extending from about 200 to 90 cm^{-1}. The details in this latter region are almost entirely obscured and lattice modes are probably the cause. It is interesting to note that a predominant absorption band occurring at about 100 cm^{-1} for fluor and hydroxyapatite is absent for the lead apatites as for chlorapatite. This band may therefore be attributed to motions involving the OH^- and F^- sublattices while the Cl^- sublattice does not give rise to such a band, or if it does it is of substantially lower intensity and therefore hidden. The masses of F^- and OH^- are about the same while that for Cl^- is approximately double and therefore the corresponding lattice mode involving Cl^- atoms might be expected to occur at much lower frequencies. A search for such a band down to 33 cm^{-1} did not reveal its presence.

The Raman spectrum for pyromorphite is given in Figure 3 and the fundamentals are tabulated in Table 3. There is a strong resemblance to the Raman spectrum of fluorapatite. The observation of the two bands at 413 and 394 cm^{-1} in the Raman spectra is consistent with our band assignment of the ν_2-bending mode in the infrared spectra. Factor-group splitting effects are certainly present as is evidenced by the lack of frequency agreement in the infrared and Raman bands. However, fewer bands appear in this spectrum than predicted by factor-group analysis or found for fluorapatite. The smaller number of bands in pyromorphite suggests that splitting effects are weaker in pyromorphite than in

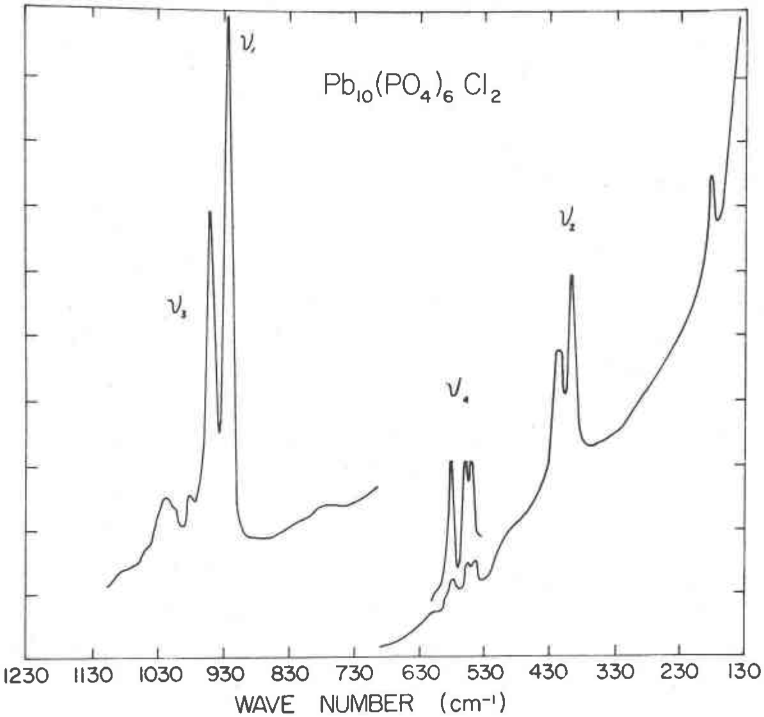


Fig. 3. The laser-Raman spectra of pyromorphite.

fluorapatite. This is reasonable since the larger Pb atoms tend to shield the PO_4^{3-}-ions more effectively from one another than the Ca atoms. In addition, the unit cell of pyromorphite is expanded relative to that of fluorapatite as can be seen by the larger lattice constants; $a = 9.364$ Å and $c = 6.879$ Å for fluorapatite while $a = 9.95$ Å and $c = 7.31$ Å for pyromorphite. Therefore, the phosphate ions in pyromorphite are physically more separated than in fluorapatite, and the force field interactions between the phosphate ions will be smaller producing smaller factor group splitting effects.

Some closely split bands were resolved by obtaining the polarized laser-Raman spectra of an oriented single-crystal of pyromorphite. A band of about 987 cm^{-1} is observed and attributed to ν_3. Thus, four out of the predicted five bands for ν_3 are observed. The band at 577 cm^{-1} is split into two bands at 576 and 584 cm^{-1} whereas the band at 541 cm^{-1} is split into two bands at 536 and 544 cm^{-1}. It, therefore, appears as though all five factor-group bands for ν_4 are present. In addition, the wide band at 413 cm^{-1} is resolved into two bands, one at 413 cm^{-1} and one at 423 cm^{-1}, revealing all three factor-group bands predicted for the ν_2 mode.

TABLE 4. BAND ASSIGNMENTS (cm^{-1}) FOR THE AsO_4^{3-}-GROUP IN MIMETITE

	AsO_4^{3-} Raman	Adler Infrared	Present Work	
			Infrared	Raman
ν_1	813		hidden	809
ν_2	342		319	341
				314
ν_3	813	800–816	814	hidden
		784	804	786
			782	766
ν_4	402		419	423
			385	412
				371

Our assignment of the low-intensity band at 436 cm^{-1} in the infrared to ν_2 is further reinforced by a consideration of factor-group effects. If the band of next lowest frequency at 245 cm^{-1} were assigned as ν_2, factor-group splitting of greater than 150 cm^{-1} would result. This would again be difficult to accept since splitting effects in the remaining fundamental modes are of the order of 2–40 cm^{-1}. Consistent with our band assignment, the ν_2 has been assigned to 420 cm^{-1} for free PO_4^{3-}-ions in solution (Steger and Herzog, 1964). Furthermore, the v_2-mode for several rare-earth phosphates is found between 460 and 493 cm^{-1} and above 400 cm^{-1} for $CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$ (Soptrajanov and Petrov, 1967; Petrov *et al.*, 1967).

Interpretation of Infrared and Laser-Raman Spectra of Mimetite. The middle and far infrared spectra of mimetite, Figure 1 and Figure 2 are similar in structure to that of pyromorphite. The band assignments of the fundamental modes are tabulated in Table 4. These assignments are made with the assumption that the weaker ν_1-mode is hidden by the ν_3-mode as was noted for Na_3AsO_4-solutions (Siebert, 1954). The remaining far-infrared spectra is poorly defined, the two prominent features being a band at 217 cm^{-1} and a very broad region of absorption centered about 134 cm^{-1}. Similarly to pyromorphite and in contrast to fluorapatite, no absorption band is found at or below 100 cm^{-1}. There are several low-intensity bands present which are ascribed to the presence of phosphate impurity in the lattice. Both chemical and spectrographic analyses reveal the presence of a small amount of phosphorous in this mimetite solid. The assignment and interpretation of these bands are consistent with those modes recently assigned by Alder (1968).

The Raman spectrum of mimetite is shown in Figure 4 with the band assignments of fundamentals collected in Table 4. The very strong band

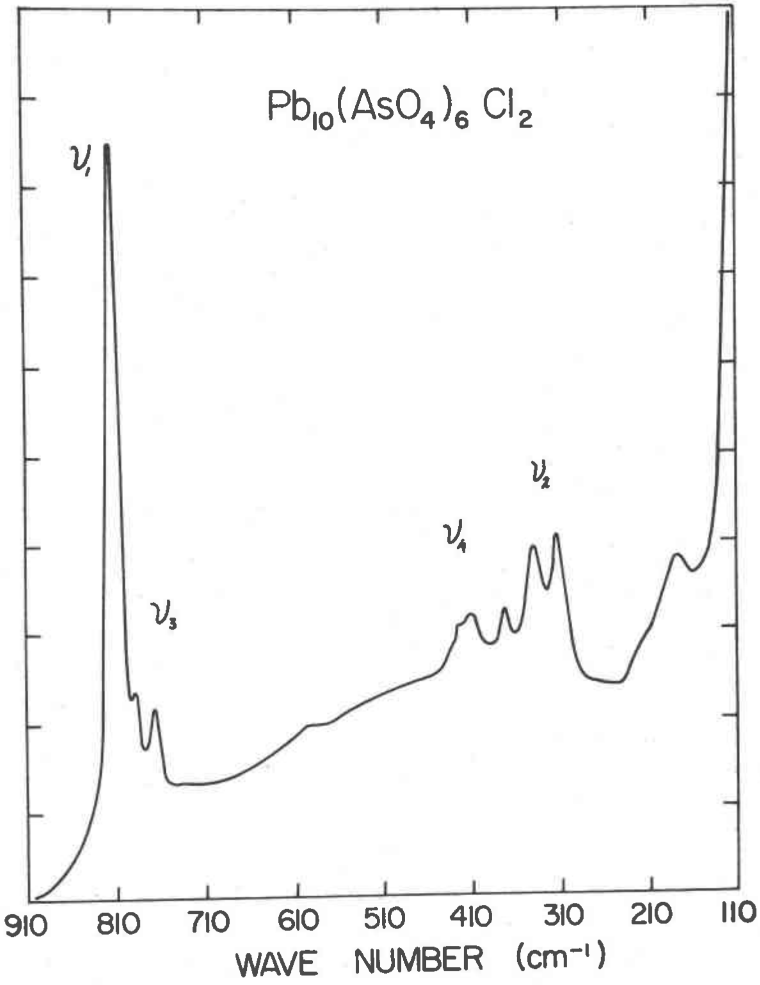


FIG. 4. The laser-Raman spectra of mimetite.

at 809 cm^{-1} is attributed to the ν_1 mode and the corresponding infrared band would be expected to occur close to this frequency. Thus the assumption of ν_1 being hidden by ν_3 in the infrared seems reasonable. Oriented single-crystal results show the band at 809 cm^{-1} to shift by a few wave numbers for different orientations indicating that there may be another unresolved band at this location. This unresolved band is assumed to be one of the factor-group components of ν_3, but it is possible that it might be the second component of ν_1 predicted by factor-group analysis. Two bands at 786 and 766 cm^{-1} are associated with factor-group bands due to ν_3 and there is now a convergence of ν_1 and ν_3 locations. Similarly, ν_2 and ν_4 components have converged on one another making their assignments difficult without further experimental determinations. However, on the basis of similarity of location and intensity with respect to pyromorphite and fluorapatite, the three bands at 423, 412 and 371 cm^{-1} are assigned as factor-group components of ν_4 and the two bands at 341 and 314 cm^{-1} to factor-group components of ν_2. The lack of frequency agreement between the infrared and Raman bands again indicates factor-group effects are occurring. Again fewer bands are observed than expected indicating smaller coupling effects for this lead apatite than for the calcium apatites. No additional resolution was achieved with oriented single-crystals. The unit cell of mimetite is slightly expanded relative to pyromorphite, and thus smaller splitting effects might be expected to occur in the mimetite lattice. The proximity of the major bands in the infrared and Raman lend confidence to their assignment as components of fundamentals. The assignment of the 319 cm^{-1} infrared band to ν_2 is again suggested by a consideration of factor-group effects. If the band of next lowest frequency at 217 cm^{-1} were assigned as ν_2, factor-group splittings of greater than 100 cm^{-1} would result. The splittings in the remaining fundamentals are of the order of 0–30 cm^{-1} and thus the higher-frequency band at 319 cm^{-1} seems most reasonable for a ν_2 designation. It is also of interest to note that phosphate impurity bands do not appear in the Raman spectrum. This is reasonable since the Raman effect is rather weak and species of such low concentration would not be expected to appear. Of further interest is the fact that the ν_1 Raman band occurs at a higher frequency than the components of ν_3. This effect is unexpected from previous infrared results on mimetite and may be closely related to a similar effect reported for VO_4^{3-} ions in solution. Recently, Krebs and Müller (1967) have carried out a normal coordinate analysis on the spectra of VO_4^{3-} in solution, using a UBF-field, and noted that the large magnitude of the O · · · O nonbonded force constant of the VO_4^{3-} ion caused ν_1 to be larger than ν_3. A thorough normal coordinate analysis and associated potential-energy distribution analysis could indicate whether this is the mechanism that influences the ν_1/ν_3-ratio for mimetite.

Interpretation of Infrared and Laser-Raman Spectra of Vanadinite. The middle-and far-infrared spectra of vanadinite are shown in Figure 1 and Figure 2. The band assignments are tabulated in Table 5. Their overall appearance is similar to that of mimetite and pyromorphite. As in

TABLE 5. BAND ASSIGNMENTS (CM^{-1}) FOR THE VO_4^{3-} GROUP IN VANADINITE

	VO_4^{3-} Raman	Adler Infrared	Present Work	
			Infrared	Raman
ν_1	827	871	hidden	825
ν_2	340		319	321
				287
ν_3	780	801	830	hidden
		739	801	793
			737	722
ν_4	340		419	411
			383	362
			374	352

mimetite, a lower intensity sharp band characteristic of ν_1 is not observed and is assumed to be hidden by the more intense ν_3 bands. It is possible, however, that one of the bands attributed to ν_3 is in fact ν_1. The main features in the remaining far-infrared spectra are a band at 222 cm^{-1} and two very broad regions of absorption centered about 150 and 132 cm^{-1}. Again as for pyromorphite and mimetite, evidence of a predominant absorption band at or below 100 cm^{-1} is not found.

There is evidence of some phosphorous present in the vanadinite lattice as in mimetite. The low intensity bands at 998, 980 and 952 cm^{-1} are assigned as components of the phosphate ν_3 stretching mode while those at 558 and 536 cm^{-1} are assigned as components of the ν_4 bending mode. No apparent changes in the VO_4^{3-} band locations are seen when PO_4^{3-} substitutes in the lattice in varying amounts in several solids studied. A small low-intensity band at 916 cm^{-1} seen in other vanadinite specimens containing a higher concentration of phosphate impurity is attributed to ν_1. These phosphate bands occur at essentially the same location in both vanadinite and mimetite. They are all at a lower frequency than the corresponding bands in pyromorphite indicating expansion of the P to O distances when PO_4^{3-} occurs on VO_4^{3-} sites. This is reasonable, since the vanadinite unit cell is expanded relative to that of pyromorphite. If it is assumed that the frequency lowering of the phosphate bands is a measure of the expansion of the PO_4^{3-} group, then the PO_4^{3-} groups in mimetite and vanadinite are about the same size. The presence of ν_1 and the several bands attributed to ν_3 and ν_4 indicates that the PO_4^{3-} groups replacing VO_4^{3-} groups in the vanadinite solid are distorted from tetrahedral symmetry. It should also be noted that no evidence of a band at 871 cm^{-1}, previously assigned as ν_1, is observed. This assignment was made on the

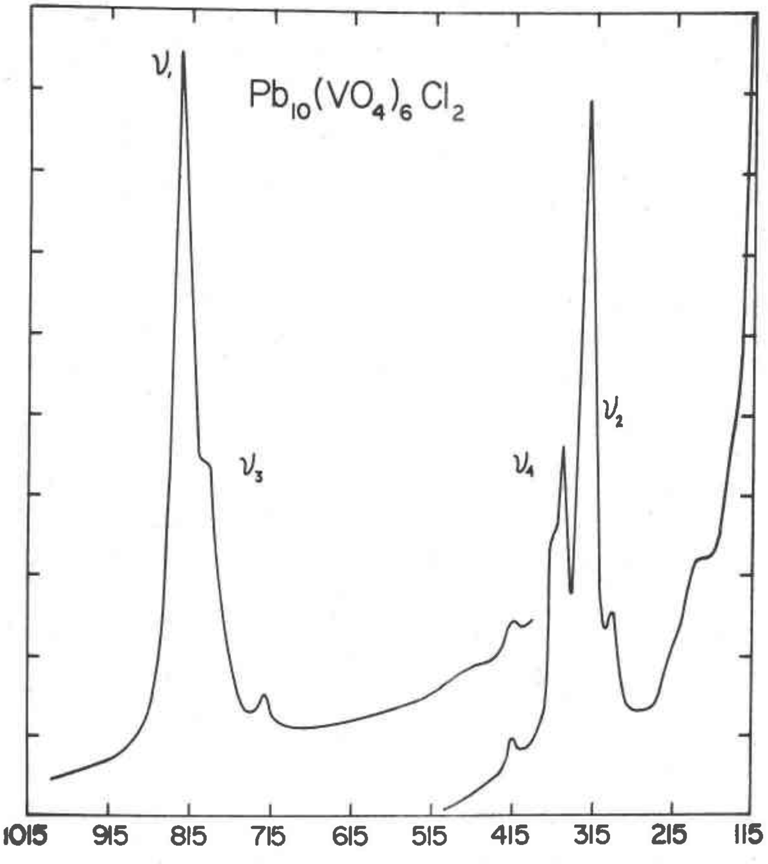


FIG. 5. The laser-Raman spectra of vanadinite.

basis of the Raman spectrum of Na_3VO_4 (Siebert, 1954) where ν_1 at 870 cm^{-1} occurs at a higher frequency than ν_3 at 825 cm^{-1}. Recently, Griffith and Wickins (1966) have shown that the above Raman results pertain to solutions containing several other species in addition to VO_4^{3-} and that ν_1 is actually found at 827 cm^{-1}. The basis for the previous assignment of ν_1 in vanadinite is in error and makes such an assignment more speculative.

The Raman spectrum of vanadinite is shown in Figure 5 and the fundamental assignments are collected in Table 5. The very strong band at 825 cm^{-1} is assigned as ν_1 and the corresponding infrared band should occur at about this location. This supports the assumption of ν_1 hidden by ν_3 in the infrared, and further, suggests that the previous assignment of ν_1 at 871 cm^{-1} is incorrect. Oriented single-crystal results show the band at 825 cm^{-1} to shift slightly for different orientations indicating the presence of a second unresolved band. As in mimetite, this hidden band is assumed to be one of the factor-group components of ν_3 but it is possible that it is the second component of ν_1 predicted by a factor-group analysis. Two bands at 793 and 722 cm^{-1} are assigned as factor-group components of ν_3. The convergence of ν_2 and ν_4, as in mimetite, is parallel to the situation found for VO_4^{3-} shown in Table 5. Again on the basis of similarity of location with respect to pyromorphite and fluorapatite the bands at 411, 362 and 352 cm^{-1} are assigned as factor-group components of ν_4 and bands at 321 and 287 cm^{-1} to factor-group components of ν_2. The presence of factor-group splitting effects is substantiated by the lack of frequency coincidence of infrared and Raman bands. The presence of fewer bands than predicted for the Raman spectra again implies coupling effects of lower degree than in the calcium apatites. Single-crystal results confirm the presence of a band at 362 cm^{-1} appearing as a shoulder in the powder Raman spectra but no other spectral details appear. Again, the assignment of the 319 cm^{-1} infrared band to ν_2 is suggested by factor-group splitting arguments similar to those of pyromorphite and mimetite. The ν_1-ν_3 frequency inversion exists as shown in the Raman spectrum for vanadinite. The present Raman spectra is the first real evidence for this inversion in vanadinite since previous assignments were made on the basis of infrared data which was incorrectly interpreted. The previous reporting of the ν_1-ν_3 inversion is thus completely fortuitous. It was earlier noted that this inversion is found also in the Raman spectrum of VO_4^{3-} in solution and was theoretically interpreted by Krebs and Müller (1967). A similar normal coordinate analysis treatment is necessary to fully understand the forces acting upon the VO_4^{3-} ion in the vanadinite lattice.

ACKNOWLEDGMENT

We are most grateful to Dr. Eugene L. Pace of Case-Western Reserve University for placing his Cary 81 Laser-Raman facilities at our disposal. Similar gratitude is owed to Dr. Richard F. Porter of Cornell University for making available his Beckman IR 11 facilities.

We also thank Dr. G. Switzer and Mr. P. E. Desautels of the U. S. National Museum for making available some of the materials used in this study. The work was supported by an NIDR research training grant (PHS Grant No. DE 00146).

REFERENCES

ADLER, H. H. (1964) Infrared spectra of phosphate minerals: symmetry and substitutional effects in the pyromorphite series. *Amer. Mineral.* **49,** 1002–1015.

——— (1968) Infrared spectra of phosphate minerals: splitting and frequency shifts associated with substitution of PO_4^{3-} for AsO_4^{3-} in mimetite. *Amer. Mineral.* **53,** 1740–1744.

GRIFFITH, W. P. AND T. D. WICKINS (1966) Raman studies on species in aqueous solutions. Part I. The vanadates. *J. Chem. Soc., A* **1966,** 1087–1090.

HENDRICKS, S. B., M. E., JEFFERSON, AND V. M. MOSLEY (1932) The crystal structure of some natural and synthetic apatite-like substances. *Z. Kristallogr* **81,** 352–369.

KRAVITZ, L. C., J. D. KINGSLEY, AND E. L ELKIN (1968) Raman and infra-red studies of coupled PO_4^{3-} vibrations *J. Chem. Phys.* **49,** 4600–4617.

KREBS, B. AND A. MÜLLER (1967) The stretching vibrations of tetrahedral XO_4^{3-}ions and oxides of transition metals with d^0-Conifurations. *Z. Chem.,* **7,** 243–244.

LEVITT, S. R. (1969) *The Vibrational Spectroscopy and Normal Coordinate Analysis of Geological Apatites.* Ph.D. Thesis, S.U.N.Y. College of Ceramics, Alfred University, Alfred, New York 14802.

———, AND R. A. CONDRATE (1968) The infrared and laser Raman spectra of several apatites. *23rd Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept. 3–7, 1968.*

PETROV, I. B. SOPTRAJANOV, N. FUSON, AND J. R. LAWSON (1967) Infrared investigation of dicalcium phosphate. *Spectrochem. Acta. A*, **23,** 2637–2646.

SIEBERT, H. (1954) Struktur der Sauerstoffsäuren. *Z. Anorg. Allgem. Chem.* **275,** 225–240.

SOPTRAJANOV, B. AND I. PETROV (1967) On the structure and symmetry of the phosphate ions in some calcium phosphates. *Croat. Chem. Acta.* **39,** 37–45.

STEGER, E., AND K. HERZOG (1964) Infrarot und Raman-Spektren von Phosphatlosungen. *Z. Anorg. Allg. Chem.* **331,** 169.

TROTTER, J., AND W. H. BARNES (1958) The structure of vanadinite. *Can. Mineral.* **6,** 161–173.

WINSTON, H. AND R. S. HALFORD (1949) Motions of molecules in condensed systems: V. classification of motions and selection rules for spectra according to space symmetry. *Physica* **17,** 607–616.

YOUNG, R. A., K. SUDARSANAN, AND P. E. MACKIE (1967) Structural origin of some physical property differences among three apatites. *Int. Colloq. Solid Inorg. Phosphates,* Toulouse.

Manuscript received, January 30, 1970; accepted for publication, April 17, 1970.