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Observation of a Phase Transition in $ThBr_4$ and $ThCl_4$ Single Crystals by Far-Infrared and Raman Spectroscopy Study

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At 4 K the visible and infrared absorption and emission spectra of U^{4+} in $ThBr_4$ and $ThCl_4$ single crystals are not very consistent with what is predicted by the selection rules for the room temperature structure. Thus we investigated Raman scattering in the temperature range 10–300 K to look for a structure change and obtain a better understanding of the spectroscopy of U^{4+} in $ThBr_4$ and $ThCl_4$. At room temperature, the observed Raman lines have been assigned on the basis of a D_{4h} factor group analysis. The study of the temperature dependence of the Raman spectra permitted us to discover phase transitions of $ThBr_4$ and $ThCl_4$ at 95 and 70 K, respectively. The splitting observed for the strongest E_g symmetry mode shows a lowering of the symmetry below the transition point. Powder X-ray diffraction at 77 K of hygroscopic $ThBr_4$ is being carried out to determine the low-temperature structure.

I. Introduction

Thorium tetrachloride and thorium tetrabromide are new host materials for tetravalent ions (*1*) such as the actinide ions for which spectroscopic properties are not well known. Thorium tetrachloride has two well-established crystalline forms with a $\beta \rightarrow \alpha$ transformation within the temperature range 320–435 °C. β-$ThCl_4$ has a D_{4h}^{19} tetragonal structure (*2–4*). According to d'Eye (*5*), $ThBr_4$ is isostructural with β-$ThCl_4$ and UCl_4. A transformation $\beta \rightarrow \alpha$ by heating samples at 330 °C has been observed by Scaife (*6*). In a recent study, Brown, *et al.* (*7*) used qualitative X-ray powder data to examine $ThBr_4$ and were unable to find any evidence of the (α) form of $ThBr_4$. Further, Mason *et al.* (*8*) tried to determine if polymorphism exists in $ThBr_4$ and proved also the existence of the α form but with a structure different from that found by Scaife. In our case, we verify on the basis of X-ray powder diffraction data that $ThBr_4$ and $ThCl_4$ single crystals have D_{4h}^{19} tetragonal structure (β form) at room temperature. Thus we will not discuss in this paper the nature of the α form but we will point out a new phase transition at very low temperature determined by Raman techniques.

In a D_{4h}^{19} tetragonal structure, the Th^{4+} ion

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is at a site of D_{2d} symmetry and the tetrapositive actinide ions substitute into this site. So we studied first the optical properties of U^{4+} (*1*) in these matrices since the f^2 configuration is the simplest case. Using the crystal field model there are more energy levels than parameters. In order to assign U^{4+} electronic levels, absorption and emission spectra of U^{4+} in $ThBr_4$ and $ThCl_4$ have been recorded at 4 K. However, the spectra consist of many more lines than could be reasonably attributed to zero phonon electronic transition (*1, 9*).

In order to distinguish between vibronic and pure electronic transition and to study what happens in the structure when the temperature decreases from room temperature to liquid helium temperature, we have investigated the Raman scattering and far-infrared absorption of $ThBr_4$ and $ThCl_4$.

2. Experimental

Thorium tetrabromide and tetrachloride were prepared at Orsay by direct reaction of thorium metal and bromine or chlorine at 900°C (*10*). As $ThBr_4$ and $ThCl_4$ are hygroscopic, the material was transferred to a crystal growing silica tube in an inert-atmosphere dry box. Single crystals of $ThBr_2$ cleave readily perpendicular to the optical axis; therefore, it is difficult to obtain a large piece that includes the optical axis. This presented no great problem for the polarized Raman experiments as the laser spot was very small. It did, however, make difficult the recording of the far-infrared reflectivity and as a result we have only measured one polarization.

Measurements of the Infrared Spectra

Far-infrared absorption measurements were made at room temperature in the region 400–20 cm^{-1}, with a Grubb Parsons-type interferometer. The samples were fine powders of $ThBr_4$ and $ThCl_4$ pressed into polyethylene pellets.

Infrared reflection spectra were recorded on the same apparatus. The $ThBr_4$ sample was a single crystal, 5 mm square, with the cleavage plane polished.

Measurements of the Raman Spectra

Raman spectra were obtained with a Jobin–Yvon Ramanor HG2S double monochromator equipped with holographic gratings, and lock-in detection techniques were used. All spectra were recorded in polarized light, using right-angle geometry. The exciting lines were provided by a 10-W Spectra Physics cw Ar ion laser. Low-temperature experiments were performed with a conduction cryostat operating between 8 and 300 K.

3. Results and Discussion

$ThBr_4$ and $ThCl_4$ are reported as being isostructural (*7*) having the space group $D_{4h}^{19} - I_{4_1/amd}$ ($Z = 2$). To perform the analysis, we have first assumed that the $ThBr_4$ and $ThCl_4$ crystals were essentially

TABLE I

FACTOR GROUP ANALYSIS FOR $ThBr_4$ WITH SPACE GROUP D_{4h}^{19}

Representation of D_{4h}	Mode at $k = 0$ Acoustic	Mode at $k = 0$ Optic	Selection rule
A_{1g}	0	2	$x^2 + y^2, z^2$ Raman
A_{2g}	0	1	Inactive
B_{1g}	0	1	$x^2 - y^2$ Raman
B_{2g}	0	3	xy Raman
E_g	0	4	(xz, yz) Raman
A_{1u}	0	1	Inactive
A_{2u}	1	2	z ir
B_{1u}	0	1	Inactive
B_{2u}	0	2	Inactive
E_u	1	3	(x, y) ir

ionic. Table I gives a factor group analysis of the proposed structure with two molecules per primitive unit cell. It can be seen that the number and symmetry species of the optically active internal mode may be given by the following representations:

$$\Gamma_{\text{internal}} = 2A_{1g} + A_{2g} + B_{1g} + 3B_{2g} + 4E_g + A_{1u} + 2A_{2u} + B_{1u} + 2B_{2u} + 3E_u$$

Table I shows that only $2A_{2u}$ and $3E_u$ vibrations will be ir active crystal modes and $2A_{1g} + B_{1g} + 3B_{2g} + 4E_g$ vibrations will be Raman active.

Assignment of the Infrared Transmittance and Reflectance Spectra

Because of the difficulty in the sample thickness far-infrared spectra were obtained on crystalline powders of $ThBr_4$ and $ThCl_4$. The spectra in the range 80–20 cm^{-1} and 400–80 cm^{-1} are reported in Fig. 1 for $ThBr_4$, $ThBr_2$:U^{4+} (doped with 1%), and $ThCl_4$. Here, four bands are observed at 70, 98, 125, and 160 cm^{-1} for $ThBr_4$ and $ThBr_4$:U^{4+} and at 103, 134, 162, and 230 cm^{-1} for $ThCl_4$. The tetravalent uranium ion radius is about the same as that of thorium, so the addition of some uranium does not disturb the vibration frequencies of the matrix. The band which appears at about 90 cm^{-1} has been attributed to hydrated $ThBr_4$.

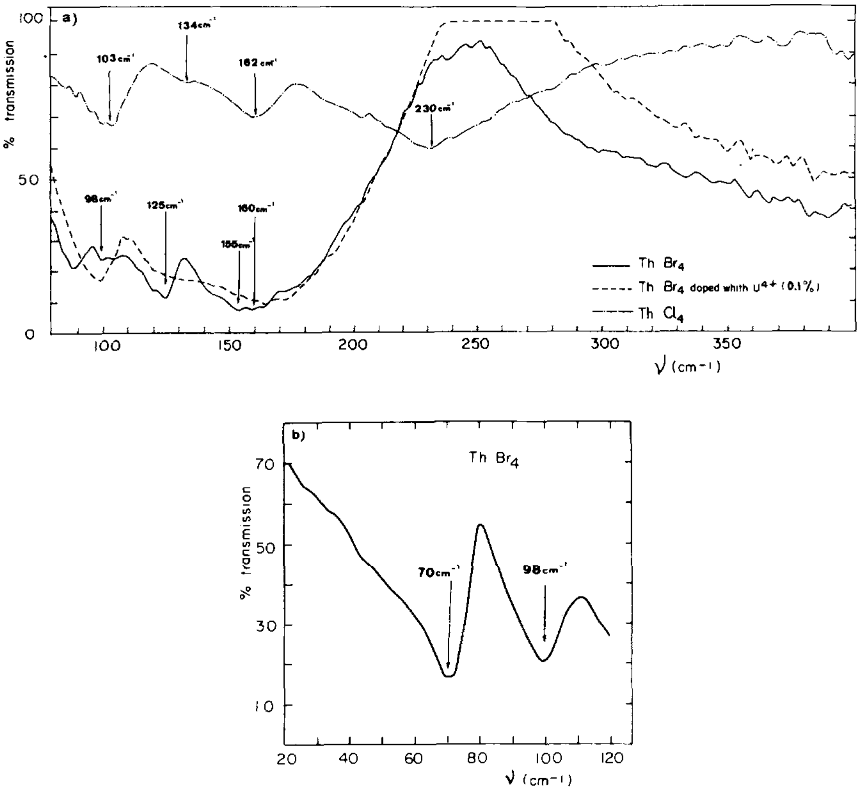

FIG. 1. Far-ir absorption spectrum of $ThBr_4$ and $ThCl_4$ at room temperature: (a) range 80–400 cm^{-1}; (b) range 20–80 cm^{-1}.

Difficulties occur in assignment of the observed bands because all orientations are possible in the powder. However, taking into account the D_{4h}^{19} space group, five modes are active. So it will be assumed that the broad band in the range near 160 cm^{-1} may contain two bands, the first one at about 155 cm^{-1} and the other one at 160 cm^{-1} for $ThBr_4$. For $ThCl_4$, this band is also very broad, and the decomposition is less noticeable.

In order to substantiate this and to make the assignment of the observed bands, polarized ir reflectivity measurements were attempted on a single crystal of good optical quality $ThBr_4$. The real and imaginary parts of the complex dielectric constant ($\epsilon' = n^2 - k^2$, and $\epsilon'' = 2nk$, where n is the refractive index and k is the absorption coefficient) were obtained by transforming the reflectance data using the Kramers—Kronig analysis (*11*, *12*). The results are shown in Fig. 2. The translation optical (TO) frequencies are given by the frequency at which the imaginary part of the dielectric constant ϵ'' has maximum value and the longitudinal optical (LO) frequencies are given by the frequencies where the real part of the dielectric constant ϵ' becomes zero in changing from negative to positive values.

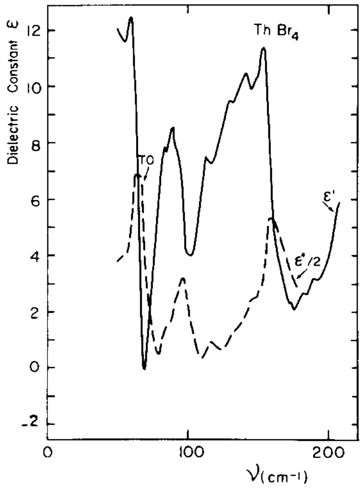

FIG. 2. The observed dielectric constant of $ThBr_4$ ϵ' and ϵ'': real and imaginary dielectric constants.

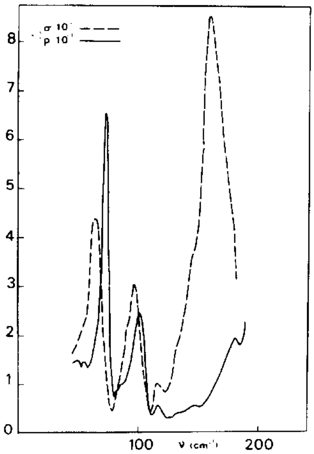

FIG. 3. The conductivity and resistivity variation versus frequency for $ThBr_4$.

Since the reflectivity was measured only for the plane which is perpendicular to the optical axis, the TO and LO frequencies obtained correspond to the E_u modes of the factor group D_{4h}.

From Fig. 2, we see only one longitudinal optical mode. In order to obtain the others, we calculated the conductivity $\sigma(\nu) = \frac{1}{2}\epsilon''\nu$ and the resistivity $\rho(\nu) = 2n''/\nu$ ($n = \epsilon^{-1} = n' - in''$). The maximum of this last function shown in Fig. 3 gives the longitudinal optical frequencies. From these data and the absorption spectra the transversal A_{2u} modes were deduced. The obtained frequencies of the E_u (TO), E_u (LO), and A_{2u} (TO) at room temperature are listed in Table II.

This study has not been made for $ThCl_4$, but we can deduce the E_u and A_{2u} modes for this single crystal by comparison with the ir absorption study of $ThBr_4$.

Assignment of the Raman Spectra

Because the crystal possesses a center of inversion, no optical modes of vibration are simultaneously Raman and infrared active.

Thus both Raman and infrared measurements are necessary to determine lattice vibrations.

The Raman spectrum is expected to consist of ten lines as reported in Table I. The polarizability tensors of these symmetries have the following form:

$$A_{1g}: \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} \qquad B_{1g}: \begin{bmatrix} c & \cdot & \cdot \\ \cdot & -c & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix} \qquad B_{2g}: \begin{bmatrix} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{bmatrix}$$

$$E_{g_1}: \begin{bmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & e \\ \cdot & e & \cdot \end{bmatrix} \qquad E_{g_2}: \begin{bmatrix} \cdot & \cdot & -e \\ \cdot & \cdot & \cdot \\ -e & \cdot & \cdot \end{bmatrix}$$

Raman spectra were recorded first at room temperature from 5 to 400 cm^{-1}, choosing the appropriate polarization for the incident and scattering light. The Raman scattering in this case was excited by the 5145-Å line. Figure 4 shows Raman spectra of the four tensor components for $\mathrm{ThBr_4}$ and $\mathrm{ThCl_4}$ oriented single crystals. The nomenclature used to denote a specific scattering geometry is that of Damen *et al.* (*13*). Table III gives the observed vibrational frequencies at room temperature and their assignments for $\mathrm{ThBr_4}$ and $\mathrm{ThCl_4}$.

So, the far-infrared and Raman study for the four scattering geometries used, at room temperature, permitted us to find the 15 vibrational active frequencies and to make assignments taking into account the

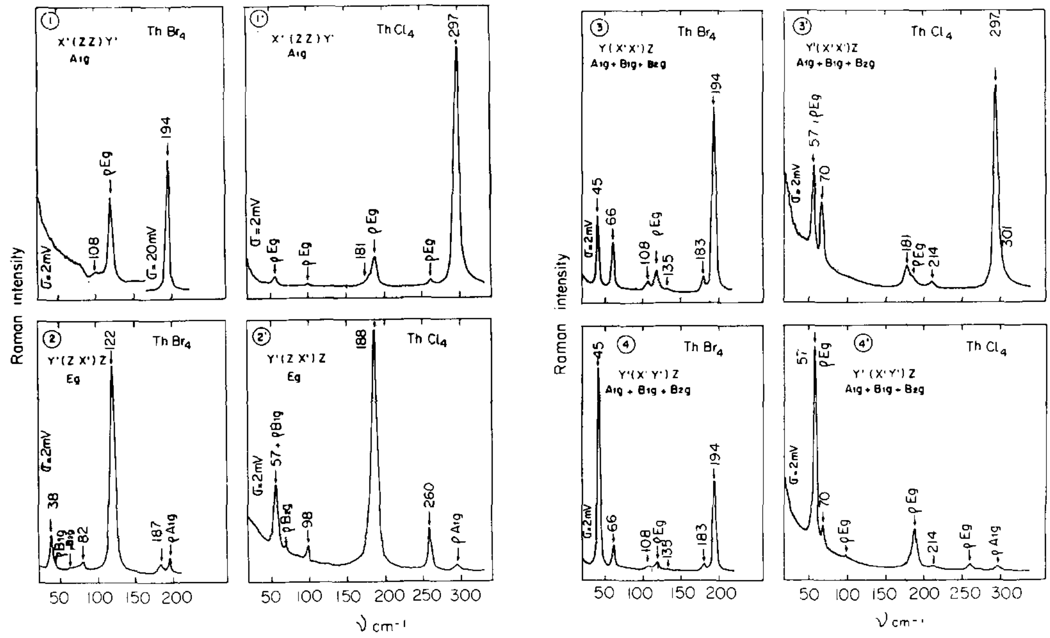

FIG. 4. Stokes Raman spectra of $\mathrm{ThBr_4}$ and $\mathrm{ThBr_4}$ at 300 K for right-angle scattering. ρ: Depolarization lines; σ: 2 mV, 20 mV sensitivity.

TABLE II

FREQUENCIES OF THE OPTICALLY INFRARED ACTIVE VIBRATIONS OF $ThBr_4$ AND $ThCl_4$ IN cm^{-1} AT ROOM TEMPERATURE

	$ThBr_4$	$ThCl_4$
E_u(TO)	66	103
E_u(LO)	73	
E_u(TO)	97	134
E_u(LO)	101	
A_{2u}(TO)	125	162
A_{2u}(TO)	155	
E_u(TO)	160	230
E_u(LO)	(180)	

space group D_{4h}^{19} for both single-crystal $ThBr_4$ and $ThCl_4$.

Until now, no Raman or far-infrared study on such single crystals has been correctly and completely analyzed. Some attempts were made on polycrystalline $ThCl_4$ powders. In these previous studies (*14*, *15*), some vibration frequencies of $ThCl_4$ were determined and are generally in agreement with our measurements. However, it should be noted that their studies were incomplete because of the poor crystalline quality of their material. Furthermore, they used the D_{2d} or T_d point group to determine the number and the symmetry of the vibration modes they observed. Under these conditions, the assignment of the vibration modes could not be made correctly.

Low-Temperature Measurement—Phase Transition Study

A far-infrared phase transition study has been attempted at temperatures of 273, 100, and 40 K, but unfortunately, the spectra observed on single crystals were not of sufficient resolution to see a change in the vibrational frequencies. Raman spectra of $ThBr_4$ and $ThCl_4$ single crystals were recorded in the temperature range 300–4 K. As the temperature is lowered, there is essentially no change in the line frequencies and no anomalous spectrum until 92 K for $ThBr_4$ and 70 K for $ThCl_4$. Below these temperatures, the spectra become very different and several additional Raman lines and splitting appeared (Fig. 5), (Table IV). This indicates a phase transition which occurs at 92 K for $ThBr_4$ and 70 K for $ThCl_4$. The splitting observed for the strongest E_g symmetry mode shows a lowering of the symmetry below the transition point, and the knowledge of this new symmetry becomes the main problem.

A better proof for the existence of a phase transition is the observation of a soft mode or unstable optical phonon. If it were so, on cooling the sample the observed temperature variation below the transition point would consist of the appearance in the low frequencies of a broad band which narrows and shifts from zero toward the higher frequencies.

In the low-temperature phase, we observed a band shifting from 5 cm^{-1} at 88 K

TABLE III

FREQUENCIES OF THE OPTICALLY RAMAN ACTIVE VIBRATIONS OF $ThBr_4$ AND $ThCl_4$ IN cm^{-1} AT ROOM TEMPERATURE

	E_g	B_{1g}	B_{2g}	E_g	A_{1g}	E_g	B_{2g}	B_{2g}	E_g	A_{1g}
$ThBr_4$	38	45	66	82	108	122	135	183	187	194
$ThCl_4$	57	57	70	98	181	188	214	301	260	297
Intensity[a]	med	str	med	wk	wk	str	wk	wk	wk	str

[a] wk—weak; med—medium; str—strong.

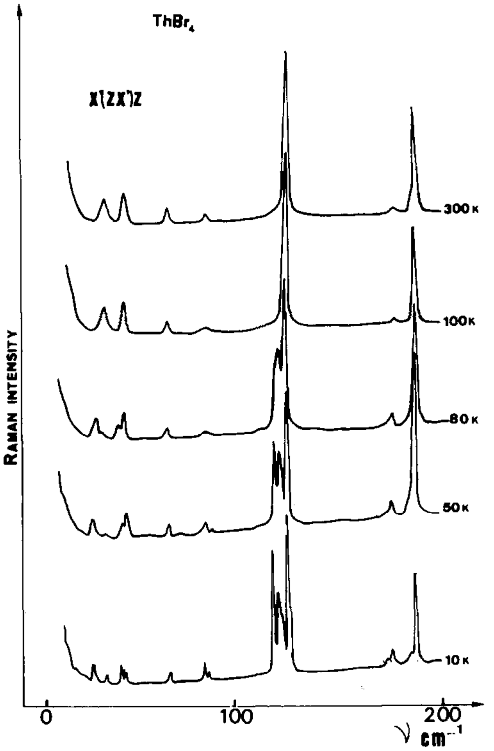

FIG. 5. Temperature dependence of part of the E_g spectrum above and below the phase transition.

to 19 cm^{-1} at 4 K. Figure 6 summarizes the ThBr$_4$ low-frequency Raman spectra at different temperatures. We can see the soft mode decrease in frequency toward zero as the phase transition was approached from below. Above the transition temperature, this mode does exist but certainly becomes Raman inactive in the D_{4h} high-temperature form. So, small deviations of the atoms from this D_{4h} symmetry can make a new Raman active mode which leads to a new low-temperature symmetry.

In the case of soft modes, we expect that the frequency ω will be proportional to $(T_c - T)^\beta$ over a substantial temperature range near the phase transition temperature T_c. To get β and T_c we plotted $\omega^{1/\beta}$ versus T (Fig. 7). From this variation we can deduce that for ThBr$_4$ the temperature dependence is given by $\omega = A(92 - T)^{1/3}$.

TABLE IV

FREQUENCIES OF THE OPTICALLY RAMAN ACTIVE VIBRATIONS OF ThBr$_4$ AND ThCl$_4$ IN cm^{-1} AT 15 K

ThBr$_4$	30 38	47 48 50	71	90 93	118	125 126 127$_{sh}$[a] 133	—	—	184	193$_{sh}$ 196
ThCl$_4$	51	63 67	75	104 107		182 187 193	214	—	265	302

[a] sh—shoulder.

4. Conclusion

The existence of a soft mode clearly demonstrates the existence of a phase transition at 92 K for ThBr$_4$ and 70 K for ThCl$_4$ that have never been seen before in these temperature ranges. The discovery of a transition

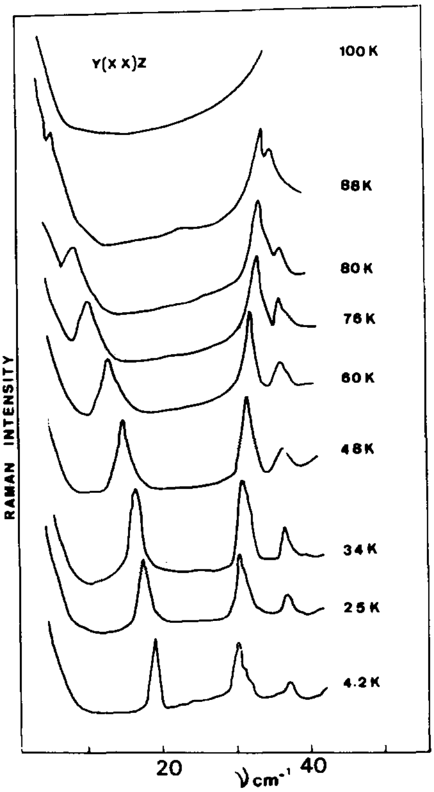

FIG. 6. Temperature variation of the polarized low-frequency Raman spectra of ThBr$_4$ (Stokes' component).

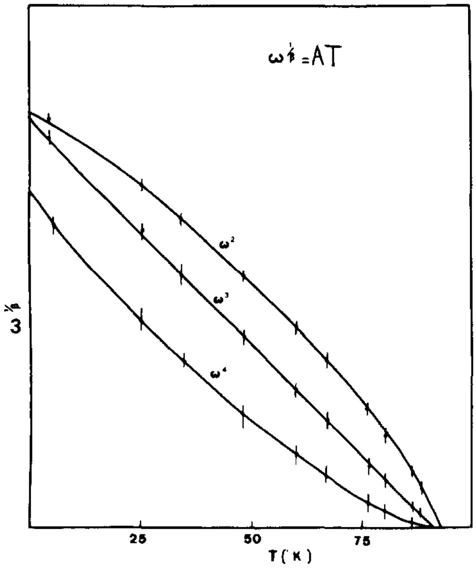

FIG. 7. Temperature dependence of the soft mode frequency.

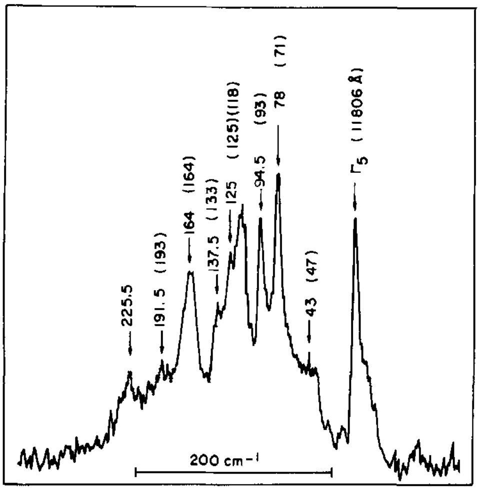

FIG. 8. Example of a vibronic spectrum associated with a zero phonon line observed in the emission spectrum of $ThBr_4 : U^{4+}$. The values in parentheses are the Raman active frequencies measured at 15 K and the ir active frequencies measured at room temperature.

phase at low temperature could explain the complexity of the electronic absorption spectra of U^{4+} (in the visible and infrared region). This fact proves the existence of a new space group at 4 K in which more than one symmetry site for Th^{4+} (and U^{4+}) can exist. Therefore a good knowledge of the fundamental lattice vibration frequencies in Raman and far infrared together could aid in the separation of vibronic transitions from pure electronic transitions of U^{4+} doped in the $ThBr_4$ and $ThCl_4$ matrices (*9*). Figure 8 shows how predicted positions corresponding to one phonon line fit experimental values. A fairly good agreement is obtained.

It is still important to know this new structure and symmetry site of U^{4+} for a better comprehension of the electronic spectra. Unfortunately no element permits us to deduce the order of the phase transition and the type of driving mechanism involved. So X-ray and neutron diffraction experiments at liquid helium temperature are now in progress. This new structure will be discussed in a further paper but what we can say using X-ray diffraction data at liquid helium temperature is that the new phase is completely different from the α form (*16*).

Acknowledgments

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