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Berg, Rolf W.; Poulsen, Finn Willy; Bjerrum, Niels

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Low temperature vibrational spectroscopy. I. Hexachlorotellurates

Rolf W. Berg,* Finn W. Poulsen, and Niels J. Bjerrum

Chemistry Department A, The Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark
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Far infrared and Raman spectra of six hexachlorotellurate (IV) salts have been obtained at ~ 100 K for the first time. In the rubidium, cesium, ammonium, and tetramethylammonium salts the Raman active T_{2g} cation lattice translatory mode was found. In the monoclinic $K_2[TeCl_6]$ a number of low frequency lattice modes were observed and interpreted in terms of a phase transition near 165 K, similar to transitions in other $K_2[MX_6]$ salts. The cubic tetramethylammonium hexachlorotellurate salt undergoes a phase transition of supposed first order at a temperature near 110 K, corresponding to transitions known in analogous uranium and tin compounds. Possible reasons for the transitions are discussed. In the low temperature phases the ν_4 and ν_6 bendings of $[TeCl_6]^{2-}$ have been identified with bands near ~ 130 and ~ 110 cm^{-1} . No evidence seemed to favor any stereochemical distortion due to the lone pair of electrons present in hexachlorotellurates.

I. INTRODUCTION

In 1957, Gillespie and Nyholm¹ developed the valence shell electron-pair repulsion theory, according to which the lone pair of electrons present in, for example, the hexachlorotellurate (IV) complex anion should be stereochemically active and distort the coordination polyhedron from being regular octahedral (Gillespie effect). However, several x-ray crystal structures of $A_2[TeX_6]$ salts (A being an alkali metal and X a halogen) have been determined,²⁻⁵ and in all cases reported so far the coordination was found to be regular octahedral at room temperature. For the hexachlorotellurate series of compounds, there is further evidence for the absence of any Gillespie effect: (i) the crystallographic equivalence of the six chlorine atoms of $(NH_4)_2[TeCl_6]$ down to liquid-nitrogen temperature shown by nuclear quadrupole resonance experiments⁶; (ii) the absence of any quadrupole splitting in ¹²⁵Te Mössbauer spectra⁷ of $Rb_2[TeCl_6]$, $Cs_2[TeCl_6]$, and $[NH_4]_2[TeCl_6]$ cooled to 80 K.

The room temperature vibrational spectra of $[TeCl_6]^{2-}$ salts have been much studied over the past decade,⁸⁻²⁰ partly owing to the considerable interest in the stereochemical properties of lone-pair compounds. Even oriented single crystal Raman spectra of $(NH_4)_2[TeCl_6]$ ¹³ and high pressure infrared spectra of a series of hexahalogenotellurate (IV) salts^{17,20} have been obtained. No low temperature vibrational results seem to have been reported for the $A_2[TeX_6]$ series, except for some bromides in the infrared.²⁰

The present work was undertaken because it was felt that combined infrared and Raman spectroscopy at low temperature performed on a series of hexachlorotellurate salts could make a valuable contribution to the understanding of the properties of hexachlorotellurate complexes both in solid and molten salts.²¹ These salts are known to have rather peculiar vibrational spectra. Generally, the Raman active $\nu_1(A_{1g})$ stretching band (Herzberg notation) is relatively weak and the infrared active $\nu_3(T_{1u})$ stretching and $\nu_4(T_{1u})$ bending bands are exceptionally strong and broad, and vanishing weak, respectively. These features of the $[TeCl_6]^{2-}$ salts differ from those seen in most spectra

of isostructural $A_2[MX_6]$ salts, as discussed in several papers,⁸⁻²¹ and various theories explaining this (including the presence of a dynamic Jahn-Teller distortion)¹⁴ have been proposed.^{14,17,18,20}

Among the compounds investigated, $K_2[TeCl_6]$ is known to have only a pseudocubic structure, a fact which has been attributed to the small size of the K^+ ion. It was found of interest to see what effect this unique structure has on the spectra during cooling. The tetramethylammonium salt was included for completeness and because low-temperature phase changes have recently been reported for similar U, Sn, and Zr compounds^{22,23} and may therefore be expected to occur in the tellurium salt as well.

In this paper we report the low temperature (~ 100 K) powder spectra of six hexachlorotellurates for the first time. For the Rb, Cs, and NH_4 salts, which retain their cubic structure down to 80 K, only minor spectral changes are seen. The same behavior is found for the thallium salt. For the K and $(CH_3)_4N$ (= tetramethylammonium) salts, remarkable changes with temperature are seen, and possible explanations for their behaviors are discussed. The results obtained add to the prevailing picture (e. g., Ref. 8, 10, and 18) of regular octahedral coordination of chlorine around tellurium, i. e., no detectable Gillespie effect.

II. STRUCTURES AND SELECTION RULES

A. Cubic compounds

The salts $A_2[TeCl_6]$ (with A = Cs, Rb, Tl, and NH_4) are known²⁻⁵ to crystallize at ambient temperature in the $K_2[PtCl_6]$ -type cubic face-centered antifluorite lattice, belonging to the space group O_h^5 ($Fm\bar{3}m$, No. 225), having one formula in the primitive cell. The lattice is illustrated in Fig. 1. Structural data for $((CH_3)_4N)_2[TeCl_6]$ are not available, but it can be assumed that this compound also adopts this type of lattice at room temperature.

For a monatomic cation, A = Cs, Rb, and Tl, the factor group expectations based on the wavevector $k \approx 0$ approximation have been derived previously, and Table I contains a summary of the results. This table also

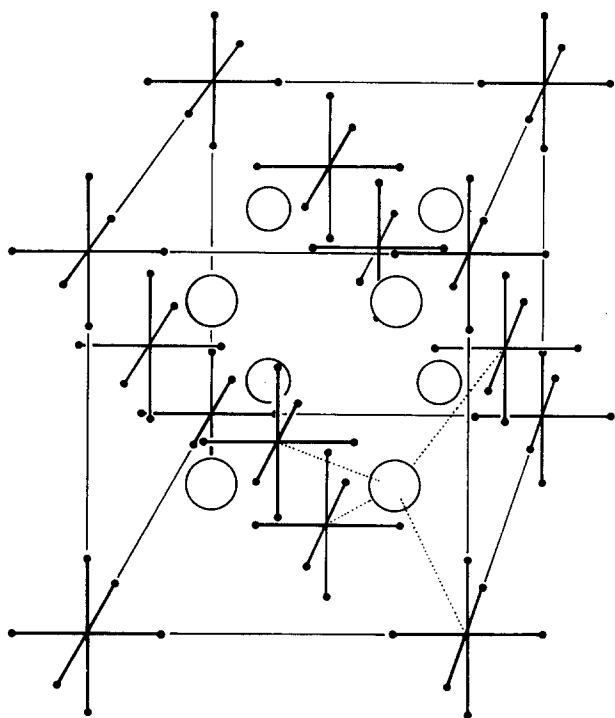


FIG. 1. Cubic unit cell of $A_2[\text{TeCl}_6]$ salts having the $K_2[\text{PtCl}_6]$ type structure.

includes the more complicated cases where A is ammonium or tetramethylammonium. Within the O_h^5 space group symmetry such tetrahedral ions can be accommodated at the cation sites c (Wyckoff notation) in two different ways, *parallel* or *perpendicular*,²² depending on whether the cation skeletal bonds point toward nearest tellurium atoms or not (cf. Fig. 1). The selection rules predicted are unaffected by the choice actually made by Nature, provided the crystal is ordered.

The cation internal modes have been omitted from Table I for the following reasons: (i) Bond stretchings and angle deformations involving hydrogen atoms occur at high frequencies compared to the spectral range of interest here, and the same is true for C–N stretchings; (ii) Methyl group torsions transform²² as $A_{2g} + T_{1g}$

TABLE I. Unit cell group analysis^a of $A_2[\text{TeCl}_6]$ salts of space group O_h^5 ($Fm\bar{3}m$, No. 225). The primitive cell contains one formula with Te on Wyckoff site a (O_h symmetry), A on site c (T_d symmetry), and Cl on site e (C_{4v} symmetry). A = Rb, Cs, NH_4 , or $(\text{CH}_3)_4\text{N}$.

O_h symmetry	T_A	T	R^-	R^+	N_i	Activity in
$A_{1g}(\Gamma_1^+)$					$1(\nu_1, \text{str.})$	Raman
$E_g(\Gamma_5^+)$					$1(\nu_2, \text{str.})$	Raman
$T_{1g}(\Gamma_4^-)$			$1(\nu_{L1})$	$1(\nu_{L4})$		
$T_{2g}(\Gamma_5^-)$		$1(\nu_{L2})$			$1(\nu_5, \text{bend.})$	Raman
$T_{1u}(\Gamma_4^-)$	1	$1(\nu_{L3})$			$2(\nu_3, \text{str.} + \nu_4, \text{bend.})$	ir
$T_{2u}(\Gamma_5^-)$				$1(\nu_{L5})$	$1(\nu_6, \text{bend.})$	

^aInternal modes of A [for NH_4 and $(\text{CH}_3)_4\text{N}$] have been omitted, see text. T_A = inactive acoustic, T = optic-branch translatory, and R^- = rotatory modes of $[\text{TeCl}_6]$, R^+ = rotatory modes of NH_4 or $(\text{CH}_3)_4\text{N}$ (where applicable), and N_i = internal modes of $[\text{TeCl}_6]$. The irreducible representations given in parentheses are solid state notation used in Refs. 28 and 29.

$+A_{1u} + T_{2u}$ and thus are all inactive under O_h (their frequencies are expected near 300 cm^{-1})²⁴; (iii) Tetramethylammonium skeletal bendings of symmetry types $E_g + E_u$ (from the E -type mode under T_d symmetry of frequency near 368 cm^{-1})^{22,25,26} and $T_{2g} + T_{1u}$ (from the T_2 -type mode under T_d occurring near 455 cm^{-1}) may be observed (E_g and T_{2g} in Raman and T_{1u} in infrared), but the frequencies are high enough to permit these modes to be clearly distinguished from the $[\text{TeCl}_6]^{2-}$ modes (ignoring the possibility of anion-cation couplings). Cation librations $T_{1g} + T_{2u}$ are inactive (Table I), and thus *no complications* due to the internal molecular structure of the NH_4 or $(\text{CH}_3)_4\text{N}$ ions are expected in the spectral range $0-350 \text{ cm}^{-1}$. Therefore, all the cubic compounds should have similar spectra; i. e., showing four bands in Raman (ν_1, ν_2, ν_5 , and ν_{L2}) and three bands in far ir (ν_3, ν_4 , and ν_{L3}).

B. Monoclinic $K_2[\text{TeCl}_6]$

The structure of this salt is incompletely solved,² but enough is known to allow a depiction of its essential structure (Fig. 2). This salt crystallizes much like the $K_2[\text{PtCl}_6]$ salt and is very nearly cubic in its parameters (C_{2h}^3 , $\beta \approx 90^\circ$, $a\sqrt{2} \approx b\sqrt{2} \approx c$)². Enough is al-

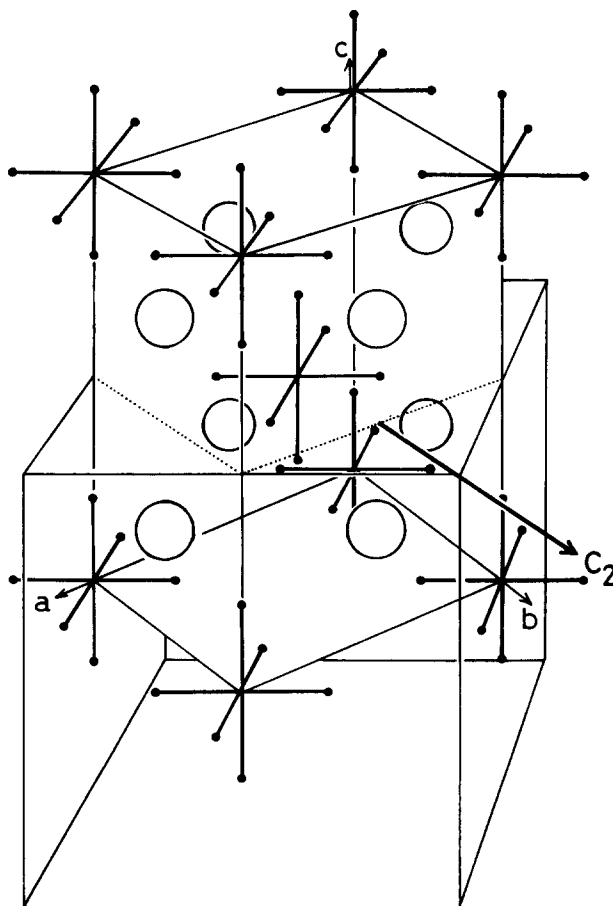


FIG. 2. The structure of $K_2[\text{TeCl}_6]$ as determined by Engel,² showing an unconventional *centered* monoclinic unit cell (of space group $C_{2h}^3(C2/m)$) which is most convenient when comparing with the $K_2[\text{PtCl}_6]$ type structure. Note the direction of the twofold symmetry axis. The positions of atoms except Te are incompletely known, cf. Table II.

TABLE II. Structural data² and unit cell group analysis^a of $K_2[TeCl_6]$ having space group C_{2h}^3 ($C2/m$, No. 12). The primitive cell contains one formula with Te on Wyckoff site a (C_{2h} symmetry), K on site i (C_s symmetry), and Cl on sites i and j (C_s and C_1 symmetries). With $a = 7.17 \text{ \AA}$, $b = 7.17 \text{ \AA}$, $c = 10.14 \text{ \AA}$, and $\beta \approx 90^\circ$, the fractional coordinates are $Te(0, 0, 0)$; $K(\sim \frac{1}{2}, 0, \sim \frac{1}{4})$, $Cl_i(\sim 0, 0, \sim \frac{1}{4})$, $Cl_j(\sim \frac{1}{4}, \frac{1}{4}, 0)$.

C_{2h} symmetry	T_A	T	R^-	N_i^b	Activity in
A_g		$2(\nu_{L2})$	$1(\nu_{L1})$	$4(\nu_1 + \nu_2 + 2\nu_5)$	Raman
B_g		$1(\nu_{L2})$	$2(\nu_{L1})$	$2(\nu_2, \nu_5)$	Raman
A_u	1	$1(\nu_{L3})$		$4(\nu_3, \nu_4, 2\nu_6)$	ir
B_u	2	$2(\nu_{L3})$		$5(2\nu_3, 2\nu_4, \nu_6)$	ir

^aFor explanation see Table I. For the correlation of the internal modes it is essential to note that one of the six interbond C_2 axes of O_h is retained as the C_2 axis in C_{2h} . The correlation scheme is then $A_{1g} \rightarrow A_g$, $E_g \rightarrow A_g + B_g$, $T_{2g} \rightarrow 2A_g + B_g$, $T_{1u} \rightarrow A_u + 2B_u$, $T_{2u} \rightarrow 2A_u + B_u$.

^bThe notation of frequencies ($\nu_1 - \nu_6$) refers to O_h symmetry, see Table I.

so known to allow the factor group analysis to be derived (Table II). Let us consider why $K_2[TeCl_6]$ is monoclinic. Engel² already attributed this to the small size of K^+ . It is instructive to compare the situation with that of $K_2[TeBr_6]$, the structure of which has been accurately determined.⁴ It is also monoclinic, though of another space group, C_{2h}^5 . $(NH_4)_2[TeBr_6]$ and $Cs_2[TeBr_6]$, on the other hand, have the cubic structure²⁷ like the chlorides. The $K_2[TeBr_6]$ structure can be considered as a cubic $K_2[PtCl_6]$ lattice in which distortions have occurred, reducing the effective size of the cation cavities.

The distortions in $K_2[TeBr_6]$ consist of the following: (i) an alternate twisting of neighboring regular octahedra about the c axis by 12° , and (ii) a twisting of all octahedra about the monoclinic b axis [cubic(110)] by 9° , followed by (iii) displacements of K^+ ions and adjustments of axial lengths and angles, leaving a structure of space group C_{2h}^5 ($P2_1/n$, No. 14, $Z=2$). For $K_2[ReCl_6]$ and $K_2[SnCl_6]$, similar twistings of type (i) have been found to occur without twistings of type (ii), making the structures of these salts noncubic.^{28,29} Other examples of distortions probably explainable along these lines are given in Ref. 4. With these results in mind, it is tempting to suggest that $K_2[TeCl_6]$ is monoclinic C_{2h}^3 due to *small* rotations of the $[TeCl_6]^{2-}$ octahedra around the [110] twofold axis in its hypothetical O_h^3 lattice. This picture accounts for the structural data²: (i) the space group becomes C_{2h}^3 {retaining the (110) mirror plane, the [110] twofold axis, and the inversion symmetry}; and (ii) the approximate atomic positions (Table II). As we shall see later, it also accounts for the spectral observations at room temperature but not at low temperature.

The vibrational consequences of the structure just described are dependent upon the magnitude of the rotation of $[TeCl_6]^{2-}$. In the limit of a vanishingly small angle, the selection rules are as given for the cubic structure (Table I). On the other hand, for an appreciable rotation the results given in Table II apply.

Assuming a maximum of splitting of the mode frequencies, it is seen that a total of 12 modes should be observed in the Raman spectrum—one ν_1 , a doublet of ν_2 , and a triplet of ν_5 (all internal modes in $[TeCl_6]^{2-}$); further, a triplet of *gerade* translatory and a triplet of rotatory modes. The infrared spectrum should contain 12 modes as well, nine of which are $[TeCl_6]^{2-}$ internals (three triplets of ν_3 , ν_4 , and ν_6) and three *ungerade* translatory modes. Qualitative mode diagrams for the internal modes of $[TeCl_6]^{2-}$ in the C_{2h} symmetry are given in Fig. 3, which has been derived by applying projection operators to a basis set of all changes in distances and angles and eliminating redundant modes. The externals (not shown) are as follows: one $A_g[TeCl_6]^{2-}$ rotation around the C_2 axis and two B_g rotations around axes perpendicular to this, further translations of the anion lattice against the cation lattice, A_u along C_2 and $2B_u$ perpendicular to C_2 , and finally *gerade* translatory movements in the cation sublattice, B_g along and $2A_g$ perpendicular to C_2 , the overall translational acoustic modes not being active in ir and Raman spectra.

It should be noted that the predictions in Tables I and II differ (apart from the static splittings due to the monoclinic crystal field) in that the silent rotatory (ν_{L1}) and bending (ν_6) modes of O_h^3 become, respectively, Raman and ir allowed in C_{2h}^3 . Finally, although the group theory shows that the triply degenerate modes of the cubic cell with split into A and B nondegenerate modes on reducing the symmetry to C_{2h}^3 , it *does not* predict the magnitude or direction of these splittings.

III. EXPERIMENTAL

An aqueous solution of ACl [$A = K, Rb, Cs, NH_4$, or $(CH_3)_4N$] was added to a solution of $TeCl_4$ ²¹ in hydrochloric acid, and the fine precipitate obtained was isolated, washed with hydrochloric acid, and dried in vacuum over silica gel. The thallium salt was prepared by melting together $TeCl_4 + 2TlCl$ in a silica ampoule. The subsequent sampling operations were done in a dry atmosphere.

The powders were mixed with polyethylene and

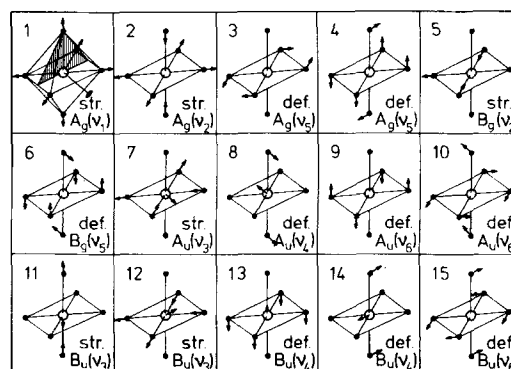


FIG. 3. Qualitative diagrams showing the 15 anion internal modes in $K_2[TeCl_6]$. In the first diagram the symmetry elements are indicated. The modes are classified as $TeCl$ stretching or bending, and their C_{2h} symmetry types and O_h origin are given.

TABLE III. Assignments and frequencies (cm^{-1}) observed for $\text{A}_2[\text{TeCl}_6]$. Underlined figures refer to ~ 100 K; in $(\text{CH}_3)_4\text{N}$ to the low temperature phase.^a

	A =	Rb	Cs	Tl	NH_4	K	$(\text{CH}_3)_4\text{N}$		
Raman	$2\nu_3$?					468, <u>475</u>			
	?						<u>301</u>		
	ν_1 (TeCl str.)	298, <u>302</u> s	290, <u>292</u> s	301, <u>303</u> s	300, <u>305</u> s	297, <u>294</u>	281, <u>284</u>		
	ν_2 (TeCl str.)	250, <u>252</u> m	248, <u>248</u> m	257, <u>257</u> m	248, <u>252</u> s	251, <u>251</u>	242, <u>244</u>		
	ν_5 (TeCl bend.)	140, <u>141</u> vs	141, <u>140</u> vs	132, <u>134</u> vs	142, <u>149</u> s	142, <u>149</u> , <u>144</u> , <u>137</u>	136, <u>143</u> , <u>136</u>		
	ν_{L2} cation translation	} 52, <u>54</u> vw	} 50, <u>51</u> vw		104 vw	109, <u>110</u>	64, <u>74</u> , <u>62</u>		
							101, <u>93</u> , <u>84</u>		
								70, <u>76</u> , <u>72</u> , <u>68</u>	
								59, <u>60</u>	
	ν_{L1} anion librations					48, <u>47</u> , <u>43</u>			
					36, <u>38</u>				
Infrared	$\nu_4 + \nu_5$?					312, <u>312</u>			
	?						290, <u>293</u> , <u>284</u>		
	ν_3 (TeCl str.)	$\sim 250, \sim 260$ vsbr	$\sim 265, \sim 260$ vsbr	$\sim 240, \sim 250$ sbr	$\sim 245, \sim 245$ vsbr	$\sim 255, \sim 255$	$\sim 230, \sim 235$		
	ν_4 (TeCl bend.)	$\sim 136, \sim 134$ vw	~ 122 vw	~ 120 vw	$\sim 140, \sim 150$ m	$\sim 140, 136, 128$	<u>120</u>		
	ν_6 (TeCl bend.)					115, <u>109</u>	<u>100</u>		
	ν_{L3} anion cation translations	66, <u>66</u> m	64, <u>66</u> m		$\sim 106, \sim 106$ m	87, <u>97</u> , <u>92</u> , <u>87</u>	75, <u>80</u> , <u>60</u>		

^aIntensity codes: vs = very strong, m = medium, vw = very weak, br = broad. For K and $(\text{CH}_3)_4\text{N}$, see Figs. 5 and 6.

pressed into discs suitable for recording far ir spectra with an RHC-FS-720/FTC-300 interferometer, equipped with a variable temperature liquid-nitrogen cryostat. The temperature of the mounting frame was measured with a thermoelement. The Raman spectra were obtained on powdered samples in glass capillary ampoules, excited by a CR500 K Kr* laser operating at 647.1 nm. The power of the beam was at the 20–80 mW level, measured after passing a narrow bandpass filter. Light scattered $\sim 90^\circ$ was collected with a lens, passed through a scrambler, and sent into a Jeol JRS-400D double monochromator equipped with concave holographic gratings (Jobin-Yvon). The signal was detected with an extended S-20 photomultiplier (HTV) at room temperature and amplified in a photon counting system. The sample temperature was controlled by means of a variable temperature liquid-nitrogen cryostat. The temperature of the copper block which surrounded the ampoule was measured with a Pt resistance thermometer. A more accurate sample temperature was estimated in several cases by ratioing Stokes and anti-Stokes intensities of bands close to the laser line.

The spectral resolution was $\sim 3 \text{ cm}^{-1}$ both in ir and in Raman. The instruments were calibrated with H_2O vapor and Kr* lines, respectively, and the vacuum wave numbers quoted are considered accurate within $\sim \pm 2 \text{ cm}^{-1}$.

IV. RESULTS AND DISCUSSION

A. General

Average tracings of the spectra obtained are reproduced in Figs. 4–6. Frequencies and assignments for the six compounds are given in Table III. Apart from small differences in band positions and shapes, the spectral features of the compounds $\text{Rb}_2[\text{TeCl}_6]$, $\text{Cs}_2[\text{TeCl}_6]$, $(\text{NH}_4)_2[\text{TeCl}_6]$, and $\text{Tl}_2[\text{TeCl}_6]$ are almost insensitive to cooling (Fig. 4). The spectra of

$(\text{CH}_3)_4\text{N}_2[\text{TeCl}_6]$ and $\text{K}_2[\text{TeCl}_6]$ show separate temperature dependent low-frequency features, (Figs. 5 and 6).

The Raman bands near the laser line ($0\text{--}200 \text{ cm}^{-1}$) have been observed in anti-Stokes scattering as well, which excluded them from being laser plasma lines. The low temperatures achieved in the far ir spectra are believed to be slightly lower than those of the Raman owing to the sample heating in the laser beam. All the observed changes in spectra with temperature were reversible.

B. Cubic compounds

The room temperature results of the literature^{10–18,20} were generally reproduced. The Raman active lattice

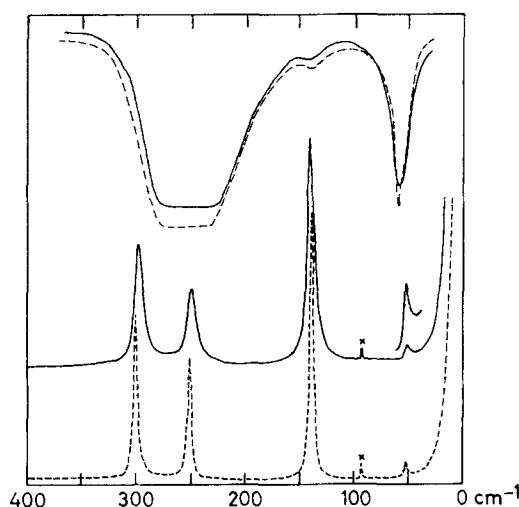


FIG. 4. $\text{Rb}_2[\text{TeCl}_6]$. Far infrared transmission spectra of powder in a pressed polyethylene disc (upper lines) and Raman scattering spectra of powder in a glass ampoule (lower lines). Solid lines: ambient temperature (~ 300 K); dashed lines: low temperature (~ 100 K). A laser plasma line marked with x occurs at 94 cm^{-1} .

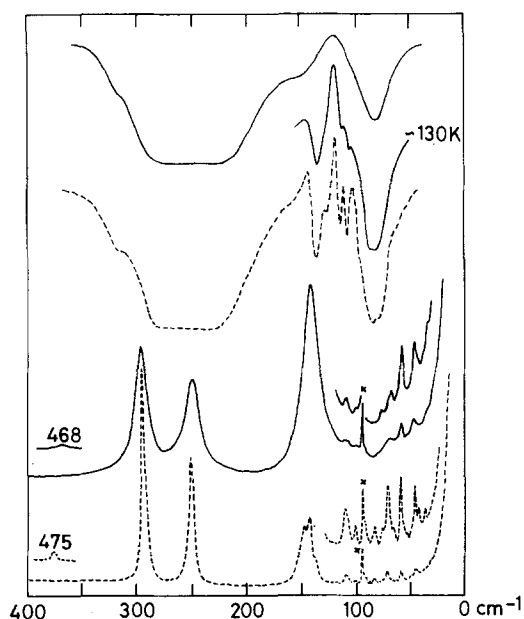


FIG. 5. $K_2[TeCl_6]$. Far infrared transmission and Raman scattering spectra. Conditions are explained in Fig. 4.

mode ν_{L2} which has never been reported before was seen in the $Rb_2[TeCl_6]$, $Cs_2[TeCl_6]$, $(NH_4)_2[TeCl_6]$, and $((CH_3)_4N)_2[TeCl_6]$ salts. In $(NH_4)_2[TeCl_6]$, ν_{L2} was observed (near 104 cm^{-1}) only at low temperature. A band at 53 cm^{-1} quoted by Hendra and Jović¹¹ could not be verified. Although the $Tl_2[TeCl_6]$ ir spectra were of poor quality, the Raman results were in accordance with previous ones,¹⁵ thus confirming the high ν_2 and low ν_5 frequencies in this compound.

Since the translational lattice vibrations are relative motions of cations and hexachlorotellurate ions (ν_{L3}) and of cations alone (ν_{L2}), their frequencies should depend strongly upon the cation mass. If the simple harmonic oscillator approximation is used, force constants can be calculated as shown in Table IV. The average value of k_{L2} ($\approx 0.16\text{ mdyn}/\text{\AA}$) will be used in the discussion on $K_2[TeCl_6]$. The rather constant value of k_{L2} and k_{L3} from crystal to crystal is indication of a small degree of coupling between translational and anion internal modes. This situation has been found previously¹⁸ and is possible, as has been shown theoretically by Gans,³⁰ even though the frequency separations between ν_5 and ν_{L2} , and ν_4 and ν_{L3} , respectively, are quite small.

C. $K_2[TeCl_6]$

Literature results^{9,10,18,20} were generally confirmed. It is evident already at room temperature that the monoclinic structure gives rise to numerous new bands; only the 88 cm^{-1} ir band and questionable ir bands at 108 and 98 cm^{-1} ¹⁰ and 70 cm^{-1} ¹⁸ have previously been reported below 135 cm^{-1} . It is possible to assign the new room temperature bands (Fig. 5) by reference to the predictions (Table II). In a reasonable approximation, the $\nu_6[TeCl_6]^{2-}$ bending mode (of symmetry species T_{2u} in a perfect octahedral configuration) should occur at a frequency $\nu_6 \approx \nu_5/\sqrt{2}$.³¹ Our ν_5 value thus

TABLE IV. Harmonic oscillator force constants $k = 4\pi^2\mu\nu^2$ for the external lattice vibrations ν_{L2} and ν_{L3} in cubic $A_2[TeCl_6]$ salts. Reduced masses $\mu_{L2} \approx M_A$ and $\mu_{L3} \approx M_{2A}M_{TeCl_6}/(M_{2A} + M_{TeCl_6})$ were used (M_A = mass of A).

A	Raman active ν_{L2} (mdyn/ \AA)	ir active ν_{L3} (mdyn/ \AA)
Rb	0.14	0.29
Cs	0.20	0.36
NH_4	0.12	0.22
$(CH_3)_4N$	0.18	0.34

gives $\nu_6 \approx 100\text{ cm}^{-1}$ in agreement with the value 103 cm^{-1} found by Adams and Morris¹⁰ using a modified Urey-Bradley force field and an estimated value of $\nu_4 \approx 139\text{ cm}^{-1}$. In the C_{2h}^3 symmetry ν_6 is ir allowed and it therefore seems reasonable to assign ν_6 to the two sharp low-temperature bands just near 100 cm^{-1} and to let ν_4 be the two bands around 140 cm^{-1} , in accordance with the commonly accepted value for ν_4 . To interpret the room temperature Raman spectrum we assumed that the approximate force constant $k_{L2} \approx 0.16\text{ mdyn}/\text{\AA}$ (just found for the cubic $A_2[TeCl_6]$ salts) also has some relevance in $K_2[TeCl_6]$. The harmonic oscillator model then gives $\nu_{L2} \approx 83\text{ cm}^{-1}$. The monoclinic field splits the cubic ν_{L2} mode into $2A_g + B_g$ (Table II), and thus it seems tempting to assign the bands at 109 and 70 cm^{-1} to cation translations ν_{L2} . Furthermore, in a work on the vibrational spectra of 31 cubic hexachloro and bromo metallates $A_2[MX_6]$, Debeau and Poulet,³² using a modified Urey-Bradley crystal force field and the method due to Shimanouchi, Tsuboi, and Miyazawa,³³ calculated the internal and external $k \approx 0$ phonon frequencies. For all the eight potassium compounds (tellurates not included), they found the external

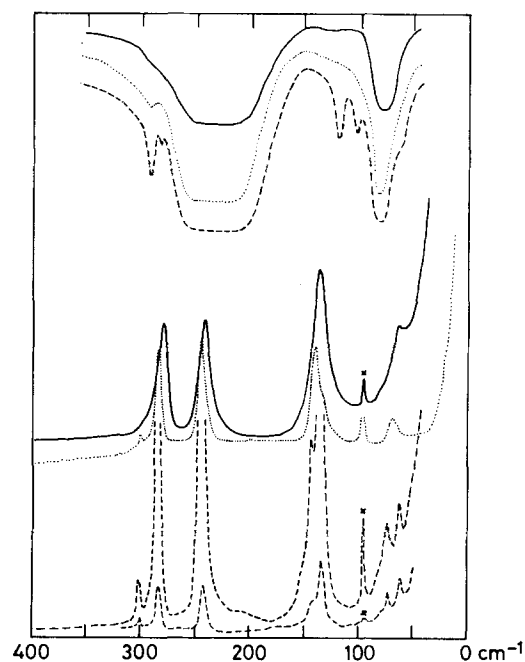


FIG. 6. $((CH_3)_4N)_2[TeCl_6]$. Far infrared transmission and Raman scattering spectra. Conditions are explained in Fig. 4. Dotted lines: low temperature ($\sim 140\text{ K}$).

frequencies to decrease in the order $\nu_{L3} > \nu_{L2} > \nu_{L1}$. Because of this we suggest that the triplet of $[\text{TeCl}_6]^{2-}$ rotational modes ν_{L1} (Table II) be assigned to the room-temperature Raman bands at 59, 48, and 36 cm^{-1} .

The low-temperature Raman spectrum of $\text{K}_2[\text{TeCl}_6]$ presents an interesting problem. According to Table II, a maximum of six different bands should occur owing to first order Raman scattering by each one of the six external lattice modes. Experimentally, 11 peaks are observed below 110 cm^{-1} (Fig. 5). Seeking an explanation for this, we considered the possibilities for second order processes. In the centrosymmetric C_{2h}^3 cell, $g \times g$ and $u \times u$ modes are probable candidates for second order Raman activity (at the Brillouin zone center Γ), and we note that bands at ~ 101 , ~ 93 , and ~ 84 cm^{-1} might arise from the combinations $38+60$, $43+60$; $43+47$, $47+47$; and $38+43$, $38+47$, $43+43$, respectively. On the other hand, it is quite difficult to explain the presence of the "wings" of the 72 cm^{-1} band and the four bands in the ν_{L1} range below 60 cm^{-1} ; longitudinal-transversal mode splitting being precluded in the centrosymmetric cell.

As a simpler explanation, we suggest the presence of a phase transition with unit cell multiplication. Should this be the case, the Brillouin zone is reduced by folding such that certain zone boundary phonons become zone center modes and therefore eventually may become Raman active by first order. It is instructive to compare this hypothesis of a phase transition with the analogous situation in $\text{K}_2[\text{PtCl}_6]$, $\text{K}_2[\text{ReCl}_6]$, and $\text{K}_2[\text{SnCl}_6]$. The first salt has no phase transitions at all.²⁸ In $\text{K}_2[\text{ReCl}_6]$, the room temperature crystal of O_h^5 symmetry is transformed three times during cooling,²⁸ probably via the space groups C_{4h}^5 and C_{4h}^4 ending up at ~ 20 K with the fourfold increased noncentrosymmetric T_h^2 cell. $\text{K}_2[\text{SnCl}_6]$ showed somewhat similar behavior.²⁹ In the low temperature (~ 10 K) Raman spectra of the Re and Sn compounds, a quite strong and sharp (and soft) ν_{L1} rotatory and a weaker ν_{L2} translatory mode were assigned^{28,29} near 30 and 80 cm^{-1} , respectively. Furthermore, bands near 60 and 90 cm^{-1} were assigned as due to $k \approx 0$ phonons (in the low temperature structure), phonons which originate from X -point phonons of the cubic Brillouin zone.

Comparing these results with our spectrum of $\text{K}_2[\text{TeCl}_6]$, which has similar bands at ~ 100 K (Fig. 6), we do not consider a cell multiplication in $\text{K}_2[\text{TeCl}_6]$ at lower temperatures as being improbable. Rather, such a phase transition would explain the quite sudden appearance of the ν_6 ir bands near ~ 165 K. These bands were just detectable at ~ 175 K and distinct at ~ 155 K (a spectrum obtained at ~ 130 K is given in Fig. 5). In this light, it is not clear whether the splitting of ν_5 depends on the phase transition or not. We have not yet investigated the Raman bands for any possible softening near ~ 165 K.

D. $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$, phase transition

It is clear from Fig. 6 that a phase transition takes place in $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ between 140 and 100 K. We had difficulties in introducing the transformation in

some samples, but it has been observed several times on different samples. Apparently the high temperature phase can sometimes be supercooled to ~ 80 K (unexposed to laser light) for hours without change. We explain it as hysteresis of transition, although it may be due to the combined effect of irradiance heating during the measurement and low cooling efficiency of our powder setup.

Averaging the ir and Raman results, the conversion temperature (T_C) is estimated to be about 110 ± 15 K. Essentially, the room temperature spectra were always observed at ~ 140 K (Fig. 6), except for small signs of what will happen during the transformation (maybe due to small unstable domains of the low temperature phase).

By means of electronic³⁴ and Raman²³ spectroscopy, similar phase transitions of quoted first order have been found near ~ 123 K in $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$, near ~ 149 K in $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$, and in $((\text{CH}_3)_4\text{N})_2[\text{ZrCl}_6]$ (T_C not known). Both the U and Sn compounds exhibited hysteresis, though not so much as found here: T_C differed up to 15 K depending on whether the determination was made with decreasing or increasing temperature. It was also found^{23,34} that the high temperature phases deviated slightly from being totally cubic O_h^5 :

(i). The electronic Laporte selection rule was violated in $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$,³⁴ hence this compound is slightly noncentrosymmetric at $T > T_C$.

(ii). The Raman spectra of the high temperature phase of both the U and Sn compound contained fundamentals which in high resolution at lower temperatures were split into close doublets, again indicating²⁸ slight deviations from the $\text{K}_2[\text{PtCl}_6]$ structure.

(iii). Adams and Morris¹⁰ reported the appearance of weak forbidden lines (in O_h^5) in x-ray powder photographs of $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$ at ambient temperature. Previously, many $((\text{CH}_3)_4\text{N})_2[\text{MX}_6]$ crystals have been shown mainly by x-ray methods to belong to the O_h^5 $\text{K}_2[\text{PtCl}_6]$ lattice; both compounds {e.g., $((\text{CH}_3)_4\text{N})_2 \times [\text{MnCl}_6]$,³⁵ $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$,³⁶ and $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$ ³⁷} having MX (metal-halogen) distances much smaller than the 2.52 Å typical for TeCl bonds^{2,5} and compounds with longer MX distances {e.g., $((\text{CH}_3)_4\text{N})_2[\text{CeCl}_6]$ ³⁸ and $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$ ³⁹}.

Preliminary Raman spectra in the range 3500–50 cm^{-1} at room temperature and at a resolution of ~ 3 cm^{-1} were measured on $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ and $((\text{CH}_3)_4\text{N})_2[\text{PtCl}_6]$, which also has a low temperature transition.⁴⁰ The spectra showed no indication of splittings of the fundamental bands, with the possible exception of the band at ~ 455 cm^{-1} . The spectra were very similar to that of $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$, obtained on powder at room temperature,²² under which conditions its known splittings were also unresolved. Hence, by analogy, we conclude that $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ may deviate slightly from being cubic at room temperature like the U, Sn, and Pt compounds, but until proved we describe it as such, in accordance with the single index of refraction (1.605) reported³⁹ for $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ crystals.

The spectra of the low temperature phase of $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ (Fig. 6) are clearly not understandable in terms of the selection rules of Table I, and hence (like for the U and Sn compounds)²³ it must have another structure, either with a lower symmetry or a larger cell. Using the data available, Ohe²³ suggested that the space group of $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$ at room temperature was D_{2d}^{11} and that the compound during the transformation is changed to have either C_{4h}^5 symmetry or a two formula unit primitive volume. Apparently, Ohe²³ did not consider the possibility in piezoelectric space groups for longitudinal-transversal splitting of modes which at the same time are ir and Raman active.⁴¹ In D_3 the E_g -type modes are both ir and Raman active, so that Ohe's observation of splittings of bands known to be of E_g type (in O_h^5) is no proof of D_{2d}^{11} being the only space group of the high temperature phase of $((\text{CH}_3)_4\text{N})_2 \times [\text{UCl}_6]$; it could equally well, for example, be D_3^3 . Evidently the $LO-TO$ splitting possibility complicates the structural derivations to a level where such deductions are not very reliable.

Instead, we therefore assumed a common reason for all the phase transitions and considered what may be unified and possible causes for the transformations. Of course, it is not known if such an assumption is justified; different things might occur in different crystals.

(i). *Cation reorientation.* The chemical literature on tetramethylammonium compounds comprises examples of crystal structures with orientationally ordered⁴²⁻⁴⁷ as well as disordered/rotating $(\text{CH}_3)_4\text{N}^+$ ions.^{48,49} Most interestingly, the x-ray structure determinations^{37,38,42} of $((\text{CH}_3)_4\text{N})_2[\text{SnCl}_6]$, $((\text{CH}_3)_4\text{N})_2 \times [\text{CeCl}_6]$, and $((\text{CH}_3)_4\text{N})_2[\text{B}_6\text{H}_6]$ (which also crystallize in the $\text{K}_2[\text{PtCl}_6]$ structure with octahedral $[\text{B}_6\text{H}_6]^{2-}$ replacing the $[\text{PtCl}_6]^{2-}$ ions)⁴² revealed the positions of the C atoms. These results indicated orientational ordering of the $(\text{CH}_3)_4\text{N}^+$ ions in the configuration named *perpendicular* by Ohe,²² and characterized by C-N bonds not pointing towards the M atoms. Presumably, this is likewise the case in other $((\text{CH}_3)_4\text{N})_2[\text{MX}_6]$ crystals. It has indeed been found also in the tetragonal distorted $((\text{CH}_3)_4\text{N})_2[\text{SiF}_6]$.⁵⁰ Then, since the $(\text{CH}_3)_4\text{N}^+$ ions are already orientationally ordered at room temperature, the transformation is not likely to be driven by the reorientational freedom of the $(\text{CH}_3)_4\text{N}^+$ ions, although the equilibrium position may be changed.

(ii). *Methyl group rotation.* The methyl groups of $(\text{CH}_3)_4\text{N}^+$ ions have been claimed to rotate quite freely around the C-N bonds in various salts,^{46,48,51} while in others they are believed^{26,42,45,52,53} to be confined to torsional oscillation (librations), sometimes around twofold disordered equilibrium positions.⁴⁷ Interestingly, $((\text{CH}_3)_4\text{N})_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ seems to contain both rotating/disordered and nonrotating/ordered methyl groups.⁴⁴ A calorimetrically detected phase transition near 406 K in $((\text{CH}_3)_4\text{N})_2[\text{B}_6\text{H}_6]$ has been assigned to the onset of methyl rotation⁴²; below that temperature the methyl groups were found fixed in the *staggered* conformation, as defined in Refs. 23 and 52. The hydrogen atoms in $(\text{CH}_3)_4\text{N}[\text{FeCl}_4]$ at room temperature seem to be con-

finied to the *staggered* conformation as well.⁴⁵ Taken together, all this x-ray diffraction evidence shows that $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ compounds might have rotating methyl groups at room and lower temperatures and that the phase transitions observed might involve the "freezing out" of one or more of these degrees of freedom. The structural change cannot be due to methyl fixation *alone*, since this probably would leave us with the *staggered*, *perpendicular* structure, which being still cubic O_h^5 cannot explain the spectra. Something else must happen.

(iii). *Weak hydrogen bonding.* It was recently demonstrated by ir spectroscopy²⁶ that the $(\text{CH}_3)_4\text{N}^+$ ion probably is able to form C-H...X hydrogen bonds to neighboring halide anions but not to, for example, $[\text{SnCl}_6]^{2-}$ and $[\text{SiF}_6]^{2-}$, at room temperature. On this basis it might be anticipated that C-H...Cl interactions, though weak, could become structurally important in $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ crystals at lower temperatures by slightly changing the packing forces and thus introducing small anisotropic distortions. Assuming $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ to be of *perpendicular* and *staggered* configuration and having the reasonable estimated lattice parameters $a \approx 13.0 \text{ \AA}$, $R(\text{Te}-\text{Cl}) \approx 2.52 \text{ \AA}$,²⁻⁵ $R(\text{C}-\text{N}) \approx 1.40 \text{ \AA}$, $R(\text{C}-\text{H}) \approx 1.09 \text{ \AA}$ and all $(\text{CH}_3)_4\text{N}^+$ angles $\approx 109.47^\circ$,^{37,38,42-50} we calculate the C-H...Cl distance to 3.8 \AA , in close agreement with the value for quoted hydrogen bonded $(\text{CH}_3)_4\text{NCl}$.²⁶ We take this as an indication of the possibility of weak hydrogen bonding in $((\text{CH}_3)_4\text{N})_2[\text{MX}_6]$ crystals at lower temperature. This might cause "freezing out" of the methyl torsions, cation displacements (e. g., along the [111] direction producing a trigonal crystal) or cation reorientation (e. g., around the z axis, reducing the symmetry to a tetragonal space group), all in order to make more efficient packing. Eventually this process may distort the T_d symmetry of the $(\text{CH}_3)_4\text{N}^+$ cations.

(iv). *Distortions of anion lattice.* As discussed for $\text{K}_2[\text{TeCl}_6]$, anion rotations or translations may change the space left for the cations. In the phase transitions of $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ crystals considered here, such distortions of the $[\text{MCl}_6]^{2-}$ sublattice might operate as well, eventually in combination with one or more of the principles discussed above. Finally, a deformation of the $[\text{MCl}_6]^{2-}$ octahedron should be considered. A possible distortion would be an elongation or compression along the directions [111] or [001], eventually in cooperation with (iii). Because of the quite close correspondence in behavior of the U, Sn, Zr, Pt, and Te compounds, we are convinced that an eventual deformation of the $[\text{TeCl}_6]^{2-}$ octahedron is unaffected by the presence of the lone pair of electrons and thus would have no relation to the Gillespie effect.¹

(v). *Analogy to the hexafluorosilicate.* It is interesting to note that the space group C_{4h}^5 deduced by Ohe²³ as a possibility for the low temperature phase of $((\text{CH}_3)_4\text{N})_2[\text{UCl}_6]$ is the same space group as that found by x-ray methods for $((\text{CH}_3)_4\text{N})_2[\text{SiF}_6]$.⁵⁰ In this tetragonally distorted antifluorite structure the $[\text{SiF}_6]^{2-}$ octahedra were all found to be rotated $\sim 34^\circ$ clockwise and the $(\text{CH}_3)_4\text{N}^+$ tetrahedra all $\sim 12^\circ$ counterclockwise,

in both cases around the z axis. The methyl groups contacted at $\sim 3.41 \text{ \AA}$ with three fluorine atoms, each from separate $[\text{SiF}_6]^{2-}$ octahedra. Each fluorine was equidistantly surrounded by four methyl groups, and the $(\text{CH}_3)_4\text{N}^+$ tetrahedra were in contact with each other. The low temperature structures of the $((\text{CH}_3)_4\text{N})_2[\text{MCl}_6]$ salts could very well be quite similar to this structure. One might object to this, that the $[\text{SiF}_6]^{2-}$ octahedron is much smaller [$R(\text{Si}-\text{F}) \approx 1.7 \text{ \AA}$]⁵⁰ than, for example, the $[\text{SnCl}_6]^{2-}$ octahedron [$R(\text{Sn}-\text{Cl}) \approx 2.4 \text{ \AA}$].²² On the other hand, it is known that, for example, $(\text{NH}_4)_2[\text{SiF}_6]$ and $((\text{CH}_3)_4\text{N})_2[\text{IrF}_6]$ are cubic at room temperature.^{54,55} As pointed out by Ohe,²³ the selection rules of a C_{4h}^5 structure are well suited to an account of the number of observed low temperature bands.

E. $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$. Spectra

As we already noted, the room temperature results of the literature^{8,10,12,20} were generally confirmed in our work. In this salt minor ir bands (at $\sim 105 \text{ cm}^{-1}$ assigned to ν_4 ^{8,10} and at $\sim 247 \text{ cm}^{-1}$ assigned to $\nu_4 + \nu_5$ ¹²) could not be verified. Instead we observed the ν_{L2} band in Raman.

We shall not attempt to assign all the *new* bands in the low temperature phase of $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ (cf. Table III), because the structure is strictly unknown and no information on the symmetry species of the bands is available. The new bands near $\sim 300 \text{ cm}^{-1}$ ($\sim 301 \text{ cm}^{-1}$ in Raman and $293, 284 \text{ cm}^{-1}$ in ir) may be due to TeCl stretchings, CH_3 rotations, or "second order" effects becoming allowed in the less symmetric or larger cell. The assignment of ν_4 and ν_6 bands were done using arguments similar to those of the $\text{K}_2[\text{TeCl}_6]$ case. Some of the bands of lowest frequency may contain intensity contributions from anion or cation librations or splitting of translatory modes as well as the tentatively assigned origin given in Table III.

V. CONCLUSIONS

No distortion of the type predicted for $[\text{TeCl}_6]^{2-}$ by Gillespie and Nyholm have been found at $\sim 100 \text{ K}$ in the six compounds investigated. The Raman active external lattice modes of T_{2g} symmetry in the antiferroite structures have been observed. Spectroscopic evidence for the presence of phase transitions at about 165 K in $\text{K}_2[\text{TeCl}_6]$ and at about 110 K in $((\text{CH}_3)_4\text{N})_2[\text{TeCl}_6]$ has been presented. In the low temperature phases the bendings ν_4 and ν_6 of the $[\text{TeCl}_6]^{2-}$ octahedron were observed at the frequencies expected. In relation to the other compounds of analogous structures we have suggested what we consider as reasonable explanations for the occurrence of the transitions. However, at the present time not enough is known about what actually occurs during the two phase transitions found here. Further work is needed to clarify the detailed nature of these transformations.

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*To whom correspondence should be sent.

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