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# Raman studies of a λ-type phase transition in solid $Cs_2CdCl_4$

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An unusual second-order-like phase transition in the perovskite-type layered compound $Cs_2CdCl_4$ has been observed by Raman studies of the solid. The phase transition took place over a range of temperatures from 435 °C to about 460 °C. At any temperature within this temperature range Raman bands characteristic of the different cadmium coordination in each of the separate phases were detected simultaneously with relative intensities that were dependent on the temperature. Analysis of the Raman spectra indicated that the structure of $Cs_2CdCl_4$ transformed from the $K_2NiF_4$-type layered-perovskite-like low-temperature phase II (octahedral cadmium coordination) to the $K_2SO_4$-type-structure high-temperature phase I (tetrahedral cadmium coordination). Relative-intensity measurements of bands characteristic of each cadmium coordination as a function of temperature indicated an equilibrium distribution. The enthalpy and entropy associated with the change of coordination were of the order of those usually observed on fusion. These large values are consistent with the major structural rearrangement from a network octahedral structure to discrete tetrahedral coordination. Although local order around the cadmium ion increased in the high-temperature phase the overall order of the lattice was considerably reduced because of the orientational disorder of the spherical, discrete $CdCl_4{}^{2-}$. Similar studies have been performed for solids of composition $Cs_2CdCl_4 \cdot 0.5CsCl$, $Cs_2CdCl_4 \cdot CsCl$, and $Cs_2CdCl_4 \cdot 2CsCl$ to follow the formation of $Cs_3CdCl_5$ which is stable above 395 °C. The presence of the peak due to $CdCl_4{}^{2-}$ at temperatures as low as 365 °C signaled the onset of the reaction to $Cs_3CdCl_5$.

## INTRODUCTION

Structural phase transitions in crystals of perovskite families have been investigated by many methods. The symmetry aspect of the phase transition in perovskitelike crystals was reviewed by Aleksandrov[1] in 1978. Scott[2,3] has reviewed the applications of light scattering. Many of the reported phase transitions have been detected below or near room temperature. Relatively few high-temperature transitions have been studied. Most of the phase transitions in the layered-perovskite-like $A_2MX_4$ crystals of the $K_2NiF_4$-type were observed in compounds with large organic cations or alkali metal, $A^+$ ions.[4] These phase transitions were found to be associated with the reordering of cations or rotation and distortion of $MX_6$ units with retention of octahedral coordination.

The low-temperature solid $Cs_2CdCl_4$ belongs to the family of the $K_2NiF_4$-type crystals.[5] The present study on the solid-state phase transition in the $Cs_2CdCl_4$ is unusual because (i) there is a change in coordination number as the structure transforms from array octahedral coordination to discrete tetrahedral species in the solid state. Usually the array octahedral network structure would only be broken on fusion but in the $Cs_2CdCl_4$ crystal, the coordination number changes from six to four at a temperature well below the melting temperature, (ii) the phase transition is associated with a dynamic equilibrium between two coordinations of cadmium over a wide range of temperatures. The transition was found to start at about 435 °C and continued until essentially completed at about 459 °C which is below the melting point of 473 °C. The presence of $CdCl_4{}^{2-}$ ions in phase II below the transition temperature can be considered a pretransition phenomenon associated with the mobility of $Cl^-$ ions. The characteristic peaks of the two cadmium coordination types coexisted over a temperature interval of about 25 °C, (iii) the formation of $Cs_3CdCl_5$ from the reaction of CsCl with $Cs_2CdCl_4$ was found to occur over a range of temperatures. The reaction began at about 365 °C and was completed at 395 °C. For mixtures of $Cs_2CdCl_4$ and $Cs_3CdCl_5$ at temperatures above 395 °C, the $Cs_2CdCl_4$ (phase II) appeared to dissolve in the $Cs_3CdCl_5$ to form a solid solution in which the cadmium is in the form of $CdCl_4{}^{2-}$ ions.

The phase transition in the $Cs_2CdCl_4$ crystal has been reported before by Seifert and Thiel[6] from x-ray and differential thermal analysis (DTA) studies. These authors reported a single phase-transition temperature of 459 °C. In a recent Raman study, Brooker and Wang[7] found evidence for the presence of tetrahedrally coordinated cadmium well below 459 °C and suggested a dynamic equilibrium between the two coordination sites of cadmium below this temperature. The results from the present Raman study indicated that the phase transition in $Cs_2CdCl_4$ was a second-order λ-type transition similar to the order-disorder transition of sodium nitrate.[8–11] In $NaNO_3$, the pretransition has been attributed to a gradual increase in the fraction of nitrate ions on disordered lattice sites. The present Raman study has an advantage over the $NaNO_3$ study[10] because the different coordination of cadmium in the two phases of $Cs_2CdCl_4$ was more easily measured than the difference between nitrates on the ordered and disordered sites of $NaNO_3$.

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## EXPERIMENT

Anhydrous $CdCl_2$ and CsCl were dried at $\sim 100\,^{\circ}C$ for a few hours under vacuum, the temperature was slowly raised to $\sim 250\,^{\circ}C$, then the samples were further dried for at least 48 h. The dried solids were handled in a dry box filled with nitrogen gas dried by $P_2O_5$. Proper amounts of $CdCl_2$ and CsCl were weighed carefully and mixed well in a mortar, then transferred into 8 mm-i.d. quartz tubes. The mixture of solids was further dried at $\sim 250\,^{\circ}C$ for 2 h under the same conditions as described above before slowly heating to the melt. The molten mixture was quenched to room temperature. The sample was transferred into a 6 mm-i.d. quartz tube and dried again at $\sim 180\,^{\circ}C$ for 2 h, then sealed under vacuum. Additional slowly cooled or quenched samples were further prepared directly in the 6 mm-i.d. quartz tubes.

Raman spectra of the solids were obtained directly from samples in the 6 mm-i.d. quartz tubes. The high-temperature studies were performed on the same samples heated in an insulated furnace with a proportional temperature controller. The temperature was monitored with a chromel-alumel thermocouple and the quoted temperature at the sample was constant to about 1 °C and accurate to about 5 °C. The observed melting points were in good agreement with the more accurate values reported by Seifert and Thiel.[6] Raman spectra were measured with a Coderg PHO Raman spectrometer. The 488.0 nm line of the argon-ion laser was used to excite the sample. The power level at the sample was about 0.3 W. Plasma lines were removed with a narrow-band-pass interference filter. A solution of 0.5 *M* Pr edetate $(EDTA)^-$ complex as a post sample filter was used to reduce stray light and ghosts. Peak positions were calibrated against the laser plasma lines. The standard 90 °C scattering geometry was used. The slit widths of the double monochromator were set at 2 $cm^{-1}$. The Raman-scattering light was detected with a photomultiplier tube (PMT) cooled to $-20\,^{\circ}C$, integrated with a photon counter and processed with a boxcar averager interfaced to the Memorial University VAX 8800 computer. Normally two data points were collected per wave number. At least two data sets were collected for each spectrum to ensure that the sample temperature was constant. Spectra were signal averaged and smoothed once with a three-point Savitsky-Golay smoothing function. A program was applied which corrected the measured intensity for the fourth-power frequency factor, and then the lowest data point was set to zero and the highest data point to 999 on a relative intensity scale. This form of the data is defined as our $I(\omega)$ spectrum which should be independent of excitation frequency. The same program was applied with the option to correct for the fourth-power scattering factor, the Bose-Einstein temperature factor $B=[1-\exp(-hc\omega/kT)]$ and the frequency factor $\omega$ to give the reduced or $R_Q(\omega)$ spectrum which is directly proportional to a point by point relative scattering activity, $S_Q(\omega)$ in terms of mass weighted normal coordinates, $Q$ in the double harmonic approximation. $R_Q(\omega)$ is the form of the Raman spectrum that most closely approaches the vibrational density of states.[12–14] The relationship between the $I(\omega)$ and $R_Q(\omega)$ forms of the spectra is given as follows:

$$S_Q(\omega) \propto R_Q(\omega) = I(\omega)\omega B \ . \tag{1}$$

For quantitative studies it is preferable to plot the spectrum in the $R_Q(\omega)$ form because the Bose-Einstein factor removes the state-dependent temperature factor of the excited-state transitions and leaves the effect that is due to concentration changes. Only in the low-frequency region are the $I(\omega)$ and $R_Q(\omega)$ significantly different and both forms are presented and discussed.

The time required to achieve equilibrium concentrations of the octahedrally and tetrahedrally coordinated cadmium dependence on the sample temperature. At lower temperatures, longer times were required. Each Raman spectrum was measured after the sample was maintained at the specific temperature long enough to ensure a constant relative intensity of the bands due to the two coordinations. Repeated measurements at a constant temperature gave identical results. Identical relative intensities were measured for samples at a given temperature for either the heating or cooling cycle.

## RESULTS AND DISCUSSION

The CsCl-$CdCl_2$ binary system has been studied by thermal and diffraction methods by Seifert and Thiel[6] and by Raman spectroscopic methods by Brooker and Wang.[7] The phase diagram is moderately complicated (Fig. 1). Five compounds have been identified; $Cs_3CdCl_5$, $Cs_2CdCl_4$, and $CsCdCl_3$ melt congruently, $Cs_3Cd_2Cl_7$

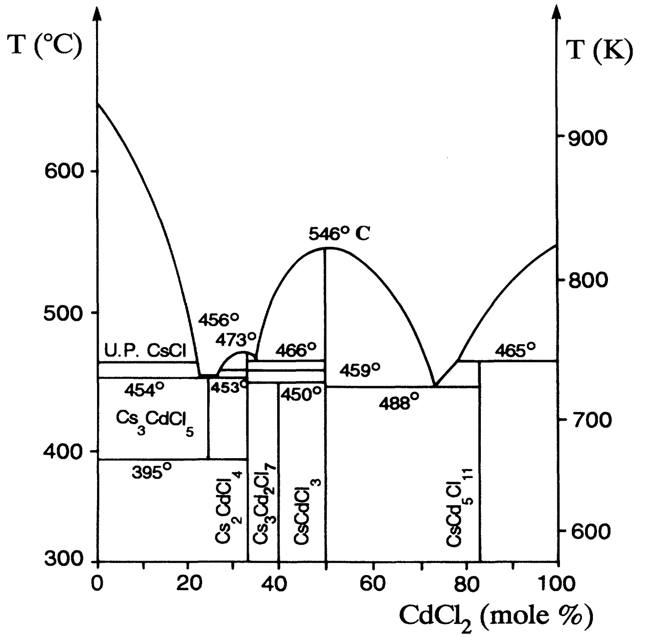

FIG. 1. The phase diagram for the $CdCl_2$/CsCl binary system which shows the phase transition at 459 °C and the formation of the stable compound $Cs_3CdCl_5$ at 395 °C. Redrawn from Ref. 6 with permission of the authors and the publisher. The temperatures indicated on the diagram are in °C.

(produced by the solid-phase reaction of $Cs_2CdCl_4$ with $CsCdCl_3$) and $CsCd_5Cl_{11}$ melt incongruently. Characteristic Raman spectra have been reported for all five compounds by Brooker and Wang.[7] $CsCdCl_3$ melts congruently at 546 °C. The crystal has a hexagonal structure and no phase transitions have been detected. $Cs_2CdCl_4$ melts congruently at 473 °C. Seifert and Thiel[6] reported that the room-temperature tetragonal structure was transformed to an orthorhombic structure at 459 °C. $Cs_3Cd_2Cl_7$ is thermodynamically stable below 450 °C and exists as a simple mechanical mixture above this temperature. However, a sample of this composition rapidly cooled from the melt to room temperature will be primarily a mixture of $CsCdCl_3$ and $Cs_2CdCl_4$ because the reaction to form $Cs_3Cd_2Cl_7$ is slow.[7] $Cs_3CdCl_5$ is a congruently melting compound that is thermodynamically stable only above 395 °C. Below 395 °C the compound decomposes into a mixture of CsCl and $Cs_2CdCl_4$. However, when $Cs_3CdCl_5$ is rapidly quenched to room temperature, the high-temperature structure can be maintained in a metastable state for a long period of time. Metastable $Cs_3CdCl_5$ decomposes into CsCl and $Cs_2CdCl_4$(II) when heated to 200 °C but reacts back to $Cs_3CdCl_5$ when heated to 395 °C.[6,7]

The composition of the $Cs_2CdCl_4$ prepared from the fused salts was checked by Raman spectroscopy.[7] Pure $Cs_2CdCl_4$ has a characteristic band at 198 $cm^{-1}$ and no other peaks in the 150 to 300 $cm^{-1}$ region. A sample of $Cs_2CdCl_4$ with excess CsCl will give rise to a Raman peak at 268 $cm^{-1}$ due to $Cs_3CdCl_5$, if the sample temperature is above 395 °C or if the sample has been quenched to room temperature from the melt. A sample of $Cs_2CdCl_4$ with insufficient CsCl will show the band at 249 $cm^{-1}$ due to the presence of $CsCdCl_3$. A band at 221 $cm^{-1}$ due to $Cs_3Cd_2Cl_7$ will also be present if the sample was cooled sufficiently slowly.

The Raman spectrum for $Cs_2CdCl_4$ at room temperature is presented in Fig. 2(a). An intense band at 198 $cm^{-1}$ and three weaker bands at 42, 69, and 92 $cm^{-1}$ have been observed (Table I). The spectrum is similar to that obtained from the isostructural compound $Rb_2CdCl_4$ as a single crystal,[4] which has four corresponding bands at 46, 85, 89, and 209 $cm^{-1}$. The vibrational spectrum of $Cs_2CdCl_4$ is in good agreement with the predictions based on x-ray studies.[5] The structure is tetragonal and isostructural with $K_2NiF_4$; space group $I_4/mmm$ $D_{4h}^{17}$. Each cadmium atom is bonded to six chloride neighbors with an octahedral local unit. Each octahedral unit is linked by sharing four corners with other octahedra to give the characteristic planes of the perovskitelike structure.

The effect of temperature on the Raman spectra for the compound $Cs_2CdCl_4$ has been measured carefully from 25 °C to above the melting point (Figs. 2 and 3; Table I). Frequencies decreased, and bandwidths increased smoothly as the temperature was increased to 435 ° C. At about 435 °C the four bands of $Cs_2CdCl_4$(II) were detected at 40, 65, 90, and 196 $cm^{-1}$. At this temperature a new set of bands appeared at 85 (shoulder), 102, and 268 $cm^{-1}$ (Table I). These bands have been assigned to the $\nu_4$, $\nu_2$, and $\nu_1$ modes of the discrete tetrahedral $CdCl_4^{2-}$ ion,

TABLE I. Raman frequencies ($cm^{-1}$) and assignments[a] for the different phases of $Cs_2CdCl_4$.

| Phase II 710 K | Phase II 298 K $D_{4h}^{17}$ | Phase I 723 K $D_{2h}^{16}$ | Melt 743 K |
|---|---|---|---|
| 40 | $42E_g$ | | |
| 65 | $69E_g$ | | |
| | | $85(sh)\nu_4$ | |
| 90 | $92A_{1g}$ | | |
| | | | $105(m,dp)\nu_2+\nu_4$ |
| | | $102(m)\nu_2$ | |
| 196 | $198A_{1g}$ | | |
| | | ··· | $255(w,dp)\nu_3$ |
| | | $268(vs)\nu_1$ | $261(vs,p)\nu_1$ |

[a] Assignments for phase II are based on the unit-cell group analysis by analogy to $Rb_2CdCl_4$ (Ref. 4) while the assignments for phase I and the melt are for the discrete $CdCl_4^{2-}$ tetrahedral ion.

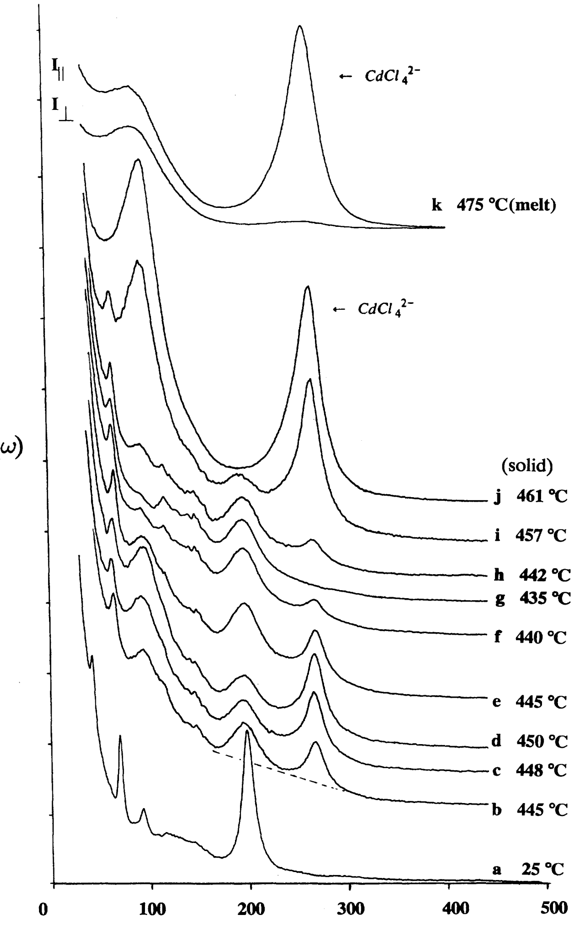

FIG. 2. Raman spectra obtained for pure $Cs_2CdCl_4$ at the temperatures indicated. Spectra were run sequentially. Spectra a–d are for the sample heated to the listed temperature; e–g for the sample cooled to the listed temperature; and h–j for the sample again heated to the listed temperature. Raman spectra (k) for the molten phase are shown for comparison with phase I (spectrum j). Slit widths were 2 $cm^{-1}$. Spectra were offset for clarity.

respectively (Table I). The band characteristic of $\nu_3$ would occur at about 260 cm$^{-1}$ but is obscured by the more intense $\nu_1$ band at 268 cm$^{-1}$. A further increase in temperature caused the intensities of the new bands to increase relative to the bands due to the low-temperature phase. The two sets of bands coexisted in the temperature range from 435 °C up to 460 °C. Above 460 °C the phase transition was complete and only the bands at 105 and 268 cm$^{-1}$ remained (Fig. 2). At about 473 °C the sample melted. The basic form of the Raman spectrum of the melt (Fig. 2) was similar to that of phase I but melting was confirmed by visual observation, abrupt changes in frequency and half-width, and the onset of polarization properties. The $\nu_1$ mode of $CdCl_4^{2-}$ at 261 cm$^{-1}$ for the melt has a depolarization ratio less than 0.1 and the $\nu_3$ mode appears at 255 cm$^{-1}$ in $I_\perp$. In the Raman $I_\parallel$ spectrum of the melt, two broad bands centered at 105 and 261 cm$^{-1}$ were observed and careful analysis indicated that the two bands result from the accidental overlap of $\nu_4$ with $\nu_2$ and $\nu_3$ with $\nu_1$ of the $CdCl_4^{2-}$ ion. At the melting point the peak maximum for the $\nu_1$ symmetric stretching mode of $CdCl_4^{2-}$ shifted abruptly from 268 cm$^{-1}$ in the solid to 261 cm$^{-1}$ in the melt and the half-width increased abruptly from 29 to 35 cm$^{-1}$. These experiments indicated that the phase transition occurred over the temperature range 435° to 460 °C and that the phase change was complete before the sample melted. There was no evidence to indicate the presence of any liquid within the solid sample below the melting point of 473 °C. The spectrum of the high-temperature form of solid $Cs_2CdCl_4$ is similar to that of solid $Cs_2MgCl_4$ which contains the discrete $MgCl_4^{2-}$ species[15] and $Cs_3CdCl_5$ which contains the discrete $CdCl_4^{2-}$ species.[7] Furthermore, the similarity of the Raman spectra observed for the high-temperature solid (phase I) and the melt suggested that there existed the same tetrahedral complex species in these two phases. These results indicated that the $Cs_2CdCl_4$ crystal transformed from the $K_2NiF_4$-type network structure with octahedral coordination of cadmium to a structure with discrete tetrahedral $CdCl_4^{2-}$ species. The new bands have been attributed to the $CdCl_4{}^{-2}$ ion in phase I (Table I).

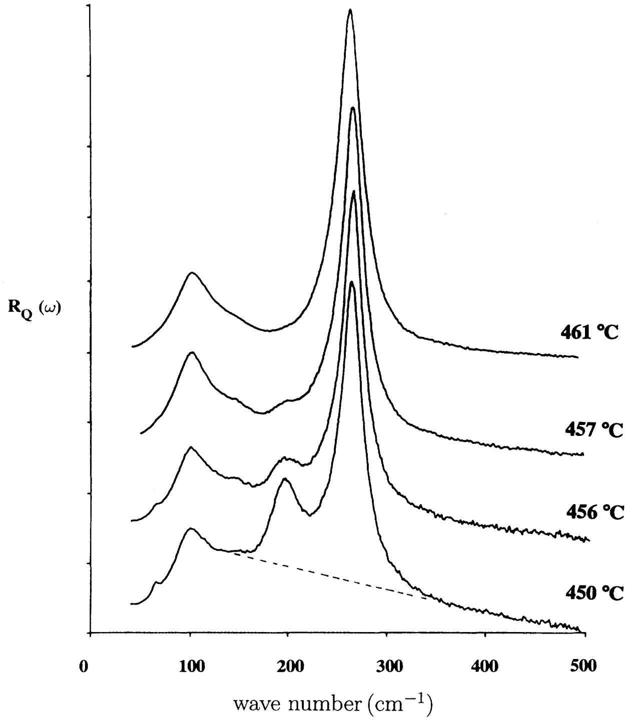

FIG. 3. Raman spectra for $Cs_2CdCl_4$ samples at the temperatures indicated with the $I(\omega)$ data (Fig. 2) normalized to the $R_Q(\omega)$ format. Spectra were offset for clarity.

The phase transition in the $Cs_2CdCl_4$ has been reported before by Seifert and Thiel[6] from the x-ray and DTA studies. The compound was reported to have a transition point at 459 °C. It was proposed that the $K_2NiF_4$-type structure with connected $CdCl_6$ octahedra transformed to the $\beta$-$K_2SO_4$-type, space group *Pnma* $D_{2h}^{16}$, with isolated tetrahedra. The measured transition enthalpy was reported to be of the same magnitude as the melting enthalpy although numerical values were not reported. It was reported that the melt undercooled by 14 °C (mp 473 °C) and at 459 °C the low-temperature modification crystallized directly. On this basis, the phase transition temperature was taken as 459 °C for the compound $Cs_2CdCl_4$. The major results of the present study are essentially in agreement with the work of Seifert and Thiel. Since DTA scan speeds are normally fast, the relatively slow pretransition phenomenon could easily be missed. Furthermore, the x-ray-powder pattern would be less sensitive to the disorder caused by the presence of $CdCl_4^{2-}$ ions in phase II.

Raman measurements in the present study indicated that almost all of the low-temperature phase had transformed to the high-temperature phase at 459 °C, but that the transition took place over a temperature range from 435 °C up to 460 °C. A dynamic equilibrium between the two coordinations of cadmium was indicated by the variation of the relative intensity of the characteristic bands due to the two solid phases as a function of the temperature. The low-temperature phase did not transform completely to the high-temperature phase at intermediate temperatures no matter how long the sample remained at a specific temperature within the temperature range. For example, identical spectra have been observed for the sample monitored over 16 h at an intermediate temperature of 440 °C. As the temperature increased, the relative intensities of the bands at 40, 65, 92, and 196 cm$^{-1}$ due to the network low-temperature phase decreased, and the bands at 268 cm$^{-1}$ and about 105 cm$^{-1}$ due to the new phase, increased. The pattern reversed as the temperature was decreased. The variation in relative intensities is illustrated for a sequence of temperatures below the phase transition (Fig. 2). These experiments indicated that the change in coordination was a reversible function of temperature.

Many studies for the phase transitions in $A_2MX_4$ and $AMX_4$ perovskite-layer-type crystals have been performed in recent years, and mechanisms have been proposed. Blinc, Zeks, and Kind[16] have proposed a model to describe the phase transition in the $(CH_3NH_3)_2CdCl_4$ compound as an orientational order-disorder transition of the $CH_3NH_3$ groups. Each $CH_3NH_3$ group has four possible equilibrium orientations in the cavities between corner-sharing $CdCl_6$ octahedra. Kind, Plesko, and Roos[17] reported that $NH_3(CH_2)_3NH_3MnCl_4$ underwent two discontinuous phase transitions at 336 and 305 K, which were governed by the rotational motion of the rigid chains around their long axes. Hidaka *et al.*[18,19] have explained the phase transition in compounds $A$FeFe$_4$ ($A$ =Rb, Cs)[18] and K$M$F$_4$ ($M$ =Fe, V, Ti)[19] as the rotations of $M$F$_6$ octahedra about the [100] and [010] axes. Electron paramagnetic resonance (EPR) studies by Aleksandrov *et al.*[4,20] suggested that $Rb_2CdCl_4$ undergoes a phase transition near 133 K. The phase transition was associated with tilts and the associated distortion of $CdCl_6$ octahedra. In all cases the mechanisms were described as reorientation of cations and/or the rotation and distortion of $MX_6$ octahedra around one or several symmetry axes in the network structure. In present case, the phase transition in the $Cs_2CdCl_4$ is unusual. The compound is the first example in the family of the $K_2NiF_4$-type crystals to have the network structure broken in the solid state at a temperature well below the melting point, with a change from octahedral to tetrahedral coordination.

In the normal phase transition,[21] such as those described above, there is a discontinuous change of entropy or volume over a very small temperature interval. Since entropy and volume are first derivatives of the chemical potential with respect to temperature and pressure, this type of transition has been classified as first order. An important criterion of the first-order transition is the fact that the observable physical properties show no sign of the impending drastic structural change. Ehrenfest and others[21] have proposed the possibility of higher-order transitions associated with second and third derivatives of the chemical potential but even true second-order transitions have been difficult to document. A number of second-order-type transitions have been reported and characterized by a gradual increase in the heat capacity up to the transition temperature followed by a rapid decline when the heat capacity falls to the value of the high-temperature phase. It is usually difficult to determine whether or not the heat capacity reaches a finite maximum (true second-order transition) or rises to infinity. This type of transition has been labeled a λ transition because of the shape of the heat capacity versus temperature plot. There is strong evidence to indicate that in the pretransition temperature region of the λ transition, the low-temperature phase and the high-temperature phase are able to coexist *along a temperature-pressure equilibrium curve* rather than just at a particular temperature and pressure.[21] The λ transition of $NaNO_3$ at about 275 °C provides a good example.[8–11,22,23] Heat-capacity measurements[8,9] have shown that the rise in heat capacity associated with the order-disorder transition begins well below the transition temperature, perhaps as low as room temperature. Mustajoki[9] reported an enthalpy and entropy of transition for $NaNO_3$ based on the arbitrary assumption that the phase transition started at 170 °C. Reinsborough and Wetmore[8] were reluctant to calculate a transition enthalpy from their heat-capacity data because of the uncertainty in the temperature at which the transition started and the inability to show that the heat capacity was finite over the transition temperature (275 °C). Diffraction[10] and spectroscopic[11,23] measurements have shown that the characteristic disorder of the high-temperature phase coexists in dynamic equilibrium within the ordered lattice of the low-temperature phase. The fraction of $NO_3^-$ ions in disordered positions increases with temperature until the interionic forces can no longer support an ordered lattice and the $NO_3^-$ ions become disordered over two equivalent lattice sites.

The results of the present Raman study indicated that $Cs_2CdCl_4$ has a λ-type transition that starts at about 435 °C and was essentially complete at 460 °C. Between 435 ° and 460 °C the low-temperature phase with $Cd^{2+}$ in an octahedral site coexisted in dynamic equilibrium with the high-temperature phase with $Cd^{2+}$ in tetrahedral sites.

In order to obtain additional information about the phase transition in $Cs_2CdCl_4$, mixtures of $Cs_2CdCl_4$ with CsCl have been studied. The mixture of $Cs_2CdCl_4$+1CsCl forms the stable compound $Cs_3CdCl_5$ above 395 °C but $Cs_3CdCl_5$ may also exist in a metastable form at room temperature.[6,7] The compound $Cs_3CdCl_5$ has been reported as isostructural[6] with $Cs_3CoCl_5$ and contains the discrete $CdCl_4^{2-}$ ion. Raman studies have indicated that the high-temperature form of $Cs_3CdCl_5$ is disordered with respect to the orientation of the $CdCl_4^{2-}$. On heating the metastable $Cs_3CdCl_5$ compound to about 200 °C, it decomposed into a mixture of $Cs_2CdCl_4$ and CsCl. Further heating of the mixture to 395 °C gave the stable form of the compound, $Cs_3CdCl_5$.

Raman spectra which illustrate the temperature dependence for the $Cs_2CdCl_4 \cdot CsCl$ mixture are presented in Fig. 4. In the temperature range from room temperature to 365 °C, the spectra are similar to those of the pure compound $Cs_2CdCl_4$(II) at a corresponding temperature. At 365 °C, a new set of bands appeared at 105 and 268 cm$^{-1}$, which appear to be due to the discrete $CdCl_4^{2-}$ ion. The intensity of the new bands increased relative to those characteristic of $Cs_2CdCl_4$(II) as the temperature increased. The two sets of the bands coexisted over a temperature range from 365 to about 390 °C when the bands due to the low-temperature phase of $Cs_2CdCl_4$ had disappeared completely. The appearance of the Raman bands characteristic of $CdCl_4^{2-}$ can be attributed to the reaction of CsCl with $Cs_2CdCl_4$(II) to form the stable compound $Cs_3CdCl_5$. It would appear that the formation of $Cs_3CdCl_5$ occurs gradually over a 25 °C temperature interval. The presence of the band at 268 cm$^{-1}$ due to $CdCl_4^{2-}$ signaled the onset of the solid-phase reaction.

Raman spectra which illustrate the temperature dependence for the $Cs_2CdCl_4 \cdot 0.5CsCl$ mixture are presented in Fig. 5. In the temperature range 370 ° to 390 °C, solid CsCl reacts with solid $Cs_2CdCl_4$(II) to form $Cs_3CdCl_5$. When the sample temperature was above 395 °C all the excess CsCl will have reacted with $Cs_2CdCl_4$ to produce

$Cs_3CdCl_5$ and the sample will consist of a mixture of $Cs_2CdCl_4$(II) and $Cs_3CdCl_5$. Above 395 °C the relative intensity of the bands due to the $CdCl_4^{2-}$ continued to increase which suggests that more $CdCl_4^{2-}$ is produced. It would appear that the $Cs_2CdCl_4$ dissolves in $Cs_3CdCl_5$ to form a solid solution with the cadmium present in the form of the tetrahedral $CdCl_4^{2-}$. When the sample temperature reached 435 °C the remainder of the $Cs_2CdCl_4$(II) gradually converted to $Cs_2CdCl_4$(I) in a similar manner to that of the pure $Cs_2CdCl_4$.

In order to confirm the unusual two-coordination equilibrium for $Cs_2CdCl_4$ a sample prepared with excess $CdCl_2$ was studied. A mixture of 3CsCl and $2CdCl_2$ can be synthesized into the incongruent compound $Cs_3Cd_2Cl_7$ (Fig. 1) under carefully controlled conditions just below 450 °C. However, normal cooling of this mixture usually results in a mixture of $Cs_2CdCl_4$, $CsCdCl_3$, and a small amount of $Cs_3Cd_2Cl_7$.[7] Raman bands at 198, 221, and 249 $cm^{-1}$, characteristic of the $Cs_2CdCl_4$, $Cs_3Cd_2Cl_7$, and $CsCdCl_3$, respectively, were observed for the sample at room temperature (Fig. 6). Raman spectra obtained for this sample at elevated temperatures indicated that the $Cs_2CdCl_4$ portion of the solid exhibited the same characteristic phase transition as the pure compound. For instance, at 370 °C the characteristic peaks for $CsCdCl_3$ and $Cs_2CdCl_4$ (phase II) were identified at 248 and 196 $cm^{-1}$, while the band at 221 $cm^{-1}$ due to $Cs_3Cd_2Cl_7$ was obscured by overlap as the 196 $cm^{-1}$ band broadened. At 440 °C a new band appeared at about 266 $cm^{-1}$ while the relative intensity of the band at 196 $cm^{-1}$ decreased (Fig. 6). The intensity of the band at 266 $cm^{-1}$ due to $CdCl_4^{2-}$ relative to that of the band at 196 $cm^{-1}$ due to $Cs_2CdCl_4$(II) was approximately the same in this 3:2 mixture as for pure $Cs_2CdCl_4$ at the same temperature. This mixture was not studied in more detail because near 450 °C the reaction between $Cs_2CdCl_4$ and $CsCdCl_3$ to produce $Cs_3Cd_2Cl_7$ proceeds more rapidly.

Studies of the intensities of the characteristic bands may further provide some quantitative information about the phase transition and the equilibrium. The relative intensities of the intense bands at 196 and 268 $cm^{-1}$ due to the two coordinations of cadmium in pure $Cs_2CdCl_4$ and mixtures of $Cs_2CdCl_4$ with CsCl were measured for samples over the temperature range of the transitions. The spectra were treated in both the $I(\omega)$ and $R_Q(\omega)$ forms as a check on internal consistency because of potential errors due to base line construction. For the $I(\omega)$ spectra,

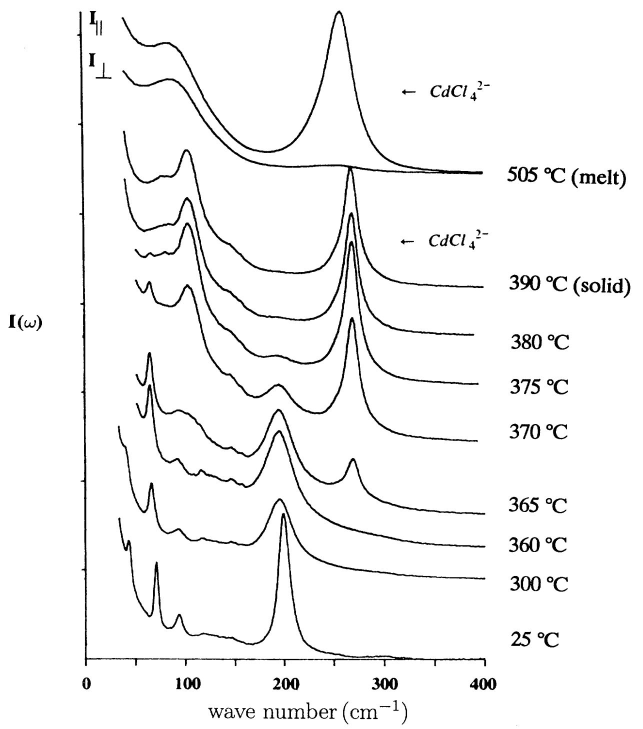

FIG. 4. Raman spectra obtained from the mixture $Cs_2CdCl_4+1CsCl$ at the temperatures indicated. The compound $Cs_3CdCl_5$ is stable above 395 °C. Spectra of the melt are shown for comparison. Slit widths were 2 $cm^{-1}$. Spectra were offset for clarity.

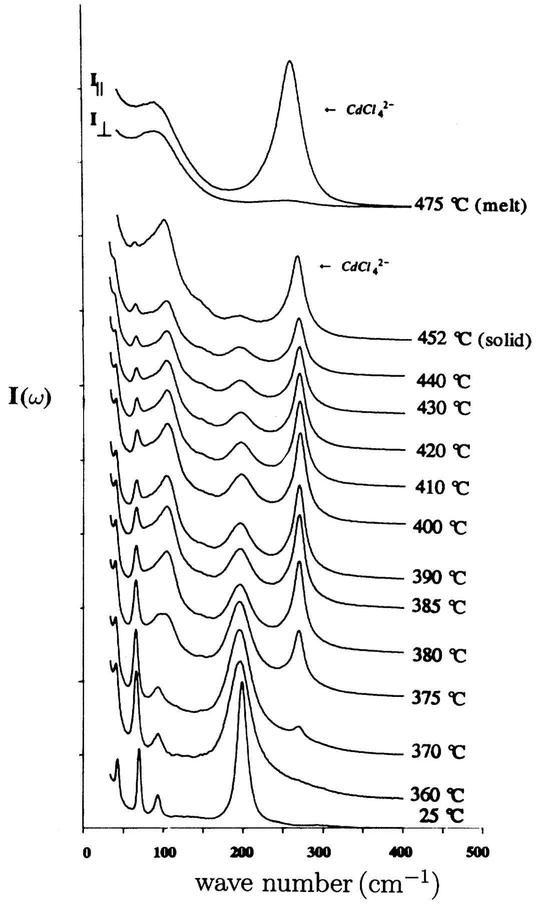

FIG. 5. Raman spectra obtained from the mixture $Cs_2CdCl_4+0.5CsCl$ at the temperatures indicated. At 370 °C the CsCl started to react with $Cs_2CdCl_4$(II) to form $CdCl_4^{2-}$ ions but by 395 °C all the excess CsCl will have been consumed to leave a mixture of $Cs_2CdCl_4$(I) and $Cs_3CdCl_5$. Slit widths were 2 $cm^{-1}$. Spectra were offset for clarity.

a level base line was achieved by numerical subtraction of a linear base line as shown (Fig. 2, 445 ° C, for example). The spectra in the $R_Q(\omega)$ format had a more level background for samples at high temperature but it was also necessary to subtract a linear base line (Fig. 3; 450 °C). The relative intensities were calculated by numerical integration and checked by the weight of paper traces. The spectra were also curve fit with two Lorentz-Gaussian product functions to provide assurance that proper base lines had been chosen and to provide an assessment of the extent of band overlap. When the relative intensities measured for the $I(\omega)$ spectra were corrected for the frequency and temperature factors, the two sets of data gave the same values (within 10%). The relative intensity data, corrected for temperature and frequency factors (Table II) provide an assessment of the relative concentrations of the octahedral and tetrahedral cadmium as a function of temperature.[13]

TABLE II. The equilibrium constants[a] calculated from Raman intensities for the two coordination types for cadmium in pure solid $Cs_2CdCl_4$ and mixtures with CsCl.

| | ln*JK* | | | |
|---|---|---|---|---|
| $Cs_2CdCl_4$ | +0.5CsCl | +1.0CsCl | +2.0CsCl | *T* (K) |
| | $-\infty$ | $-\infty$ | $-\infty$ | 633 |
| | ··· | −0.33 | −1.63 | 638 |
| | −2.65 | 1.75 | −0.36 | 643 |
| | 0.01 | 2.9 | 1.41 | 648 |
| | 0.82 | 3.8 | 3.0 | 653 |
| | 1.00 | ··· | | 658 |
| | 1.19 | ··· | 3.7 | 663 |
| | ··· | $+\infty$ | $+\infty$ | 668 |
| | 1.25 | | | 673 |
| | 1.42 | | | 683 |
| | 1.51 | | | 693 |
| $-\infty$ | 1.62 | | | 703 |
| 0,(−2.45)[b] | ··· | | | 708 |
| −0.64,(−1.51) | 1.66 | | | 713 |
| −0.36,(−0.52) | ··· | | | 715 |
| 0.37,(0.23) | ··· | | | 718 |
| 0.88 | ··· | | | 721 |
| 1.15,(1.06) | ··· | | | 723 |
| | 2.54 | | | 725 |
| 1.72 | ··· | | | 729 |
| 2.73 | ··· | | | 731 |
| $+\infty$ | $+\infty$ | | | 732 |

[a] Obtained from the intensity ratio $I_{268}/I_{196}$ for spectra corrected for the temperature and frequency factors, i.e., the $R_Q(\omega)$ spectra.

[b] Parentheses indicate a measurement made for the sample cooled to the quoted temperature.

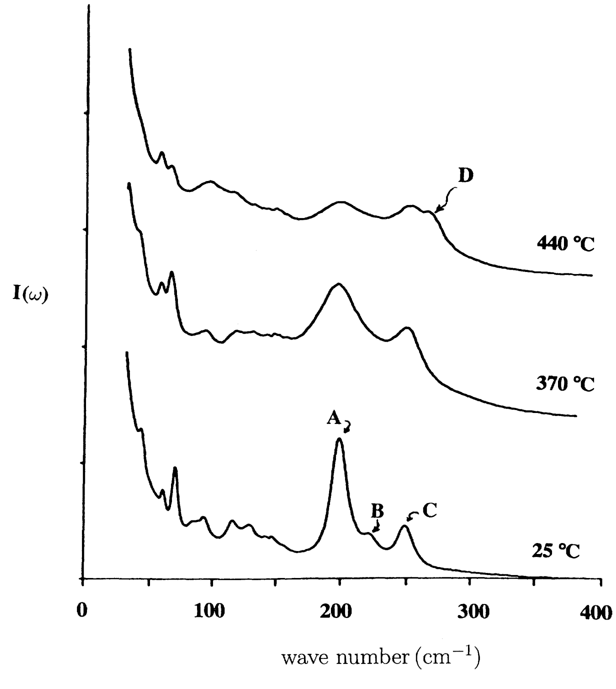

FIG. 6. Raman spectra from the solid formed from the mixture 3CsCl:2$CdCl_2$ cooled rapidly from the melt to the solid. Peak assignments: *A*: 198 cm$^{-1}$, $Cs_2CdCl_4$(II); *B*: 221 cm$^{-1}$, $Cs_3Cd_2Cl_7$, *C*: 248 cm$^{-1}$, $CsCdCl_3$; *D*: 266 cm$^{-1}$, $CdCl_4^{2-}$. The peak at 266 cm$^{-1}$ for the sample heated to 440 °C has been assigned to $CdCl_4^{2-}$ which signals the start of the transition $Cs_2CdCl_4$(II) to $Cs_2CdCl_4$(I). Slit widths were 2 cm$^{-1}$. Spectra were offset for clarity.

Within certain temperature intervals it appears that the coordination of any cadmium ion can switch from octahedral to tetrahedral with a temperature-dependent rate constant. The rate constants have not been measured but from the approximate time required for the intensity ratio to stabilize at a fixed temperature for pure $Cs_2CdCl_4$ it was possible to infer that the rate constants were of the order of hours near 430 °C and of the order of seconds near 445 °C. At a given temperature there was an equilibrium concentration of the two sites. The following ideal equilibrium was assumed:

$$\mathrm{Cd(II)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cd(I)}\ , \tag{2}$$

where Cd(II) represents the state of $Cd^{2+}$ ion with octahedral coordination in the low-temperature network structure, Cd(I) represents the state of $Cd^{2+}$ with tetrahedral coordination in the high-temperature phase, and $k_f$ and $k_r$ are rate constants.

The intensity of a Raman band is given by $I = JC$ where $J$ is the intrinsic molar scattering coefficient and $C$ is the concentration of species. At a given temperature, the intensity ratio reflects a concentration ratio,

$$\frac{I_{(268.5\ \mathrm{cm}^{-1})}}{I_{(196\ \mathrm{cm}^{-1})}} = \frac{J_{(\mathrm{I})} C_{\mathrm{Cd(I)}}}{J_{(\mathrm{II})} C_{\mathrm{Cd(II)}}} = JQ\ , \tag{3}$$

where $Q = C_{\mathrm{Cd(I)}} / C_{\mathrm{Cd(II)}}$ is a pseudoequilibrium constant (reaction quotient) of the coordination change; and $J = J_{(\mathrm{I})} / J_{(\mathrm{II})}$ is a constant.

From a kinetic viewpoint,[24] the rate constants can be expressed as follows:

$$k_f \propto \exp(-G_f^{\ddagger}/RT)\ , \tag{4}$$

$$k_r \propto \exp(-G_r^{\ddagger}/RT)\ , \tag{5}$$

and

$$Q = k_f / k_r = \exp(-\Delta G^0 / RT) \ . \qquad (6)$$

$\Delta G^0$ is a thermodynamic constant which reflects the standard change in free energy that accompanies the reaction between the two kinds of coordination referred to some standard state of the substances involved. Essentially this treatment leads to a form of the Gibbs-Helmholtz equation and suggests that a plot of ln$Q$ against $1/T$ should be linear. There are a number of problems with this type of treatment for an equilibrium in the solid phase. It was not possible to define a standard state or to evaluate activity coefficients since it was not possible to alter the equilibrium position at a constant temperature by a variation of concentration. Furthermore, the value of $J$, the ratio of the relative molar scattering factor, cannot be easily evaluated although a value of about unity can be estimated from a comparison of the relative intensity of pure phase I compared to that of pure phase II. Nevertheless, some insight about the nature of the phase transition may be inferred.

The value of $JQ$ at each temperature was determined from the ratio of the relative integrated intensities for the two bands at 268 and 196 cm$^{-1}$ for pure $Cs_2CdCl_4$ and the mixtures with CsCl (Table II). The plots of ln$JQ$ vs $1/T$ were not linear but had $S$ shapes (Fig. 7). The shapes of the curves are reasonable. For pure $Cs_2CdCl_4$ above 460 °C there is only phase I and below 435 °C there is only phase II, the value of ln$JQ$ should go to positive and negative infinity at these temperatures. For the mixture of $Cs_2CdCl_4$ and 0.5CsCl for the temperature range 390° to 440 °C the plot (Fig. 7) was almost linear and a linear regression of the six points gave a value of 4.8±0.3 K for the slope and 8.5±0.5 for the intercept. The most probable reason for the continued increase in the intensity of the band at 268 cm$^{-1}$ is that $Cs_2CdCl_4$(II) dissolves in the $Cs_3CdCl_5$ to form a solid solution. With the assumption that the heat capacity $C_p$ was constant over this temperature range it is possible to estimate values of $\Delta H$ and $\Delta S$. For the value of $\Delta S$, it was also necessary to assume that $J$ was unity since ln$J$ contributes to the value of the intercept. The values for $\Delta H$(40±3 KJ/mol$^{-1}$) and $\Delta S$(70±4 J/mol$^{-1}$K$^{-1}$) obtained in this way are clearly too large since they are as large as normal heats and entropies of fusion.[22,25] The value of $\Delta S$ obtained from $\Delta H/T$ for a transition temperature of 460 °C (55±5 J/mol$^{-1}$K$^{-1}$) is also too large. The assumption that the heat capacity would be constant is unreasonable and inconsistent with previous studies of second-order phase transitions. In fact, second-order phase transitions are accompanied by a significant increase in the value of $C_p$ up to the transition point at which temperature the value of $C_p$ usually returns over a small temperature interval to low normal values.[8,21] The $\Delta C_p$ term for the reaction would tend to decrease the values of $\Delta H$ and $\Delta S$ estimated from values of ln$JQ$. The $S$-type curve for the plot of ln$JQ$ vs $1/T$ can be considered the spectroscopic equivalent to the λ shape of the $C_p$ vs $T$ plot. Although in the present case it seems reasonable to conclude that the enthalpy and entropy of transition are probably of the same order of magnitude as those of melting as reported by Seifert and Thiel,[6] the limitations on the evaluation of these parameters preclude unambiguous evaluation. The Raman method suffers from the very same problem (i.e., the pretransition increase in $C_p$) that precludes the calculation of precise enthalpy and entropy of transition from $C_p$ vs $T$ data.

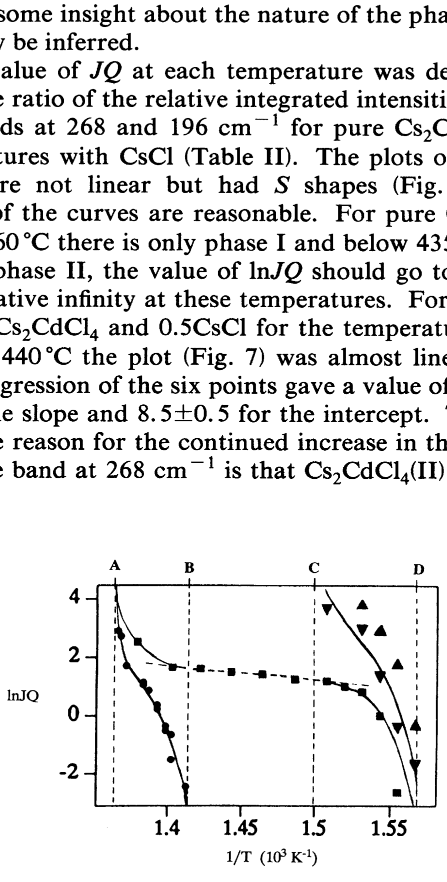

FIG. 7. The plot of ln$JQ$ vs $1/T$ for pure $Cs_2CdCl_4$ and mixtures with CsCl. $Q$ is the reaction quotient for the conversion of the octahedral to the tetrahedral coordination for cadmium, (●): pure $Cs_2CdCl_4$, (■): $Cs_2CdCl_4$+0.5CsCl, (▲): $Cs_2CdCl_4$ +1.0 CsCl, (▼): $Cs_2CdCl_4$+2.0CsCl. A: Above 459 °C the transition to $Cs_2CdCl_4$(I) is complete and all the cadmium is tetrahedrally coordinated. B: Below 435 °C the cadmium is all octahedrally coordinated in pure $Cs_2CdCl_4$(II). C: Above 395 °C the reaction of CsCl with $Cs_2CdCl_4$ is complete. D: Below 365 °C all the cadmium is octahedrally coordinated as $Cs_3CdCl_5$ reverts to $Cs_2CdCl_4$(II) and CsCl.

The large enthalpy change reflects the major structural rearrangement from the network octahedral coordination of the low-temperature phase to the discrete $CdCl_4^{2-}$ molecular ion of the high-temperature phase.

The value of $\Delta S$ is also large by comparison to entropies for many phase transitions.[22,26] For example, the entropy change is only 2.3 J/mol$^{-1}$K$^{-1}$ for the displacive phase transition of $Rb_2CdCl_4$ which involves a simple tilt of the octahedron.[4] Newns and Staveley[22] have listed the values of $\Delta S$ for phase transitions of 58 inorganic salts. The average value of $\Delta S$ was close to 10 J/mol$^{-1}$K$^{-1}$ although values as high as 33 J/mol$^{-1}$K$^{-1}$ were found. Solids with large entropies of phase transition were found to have correspondingly small entropies of fusion (and vice versa). Newns and Staveley[22] associated large entropies of transition with the onset of orientation disorder in the high-temperature phase. The magnitude of $\Delta S_{\text{trans}}$ was related to the number $n$ of equivalent distinguishable orientations available to the molecule or molecular ion, i.e., $\Delta S = R \ln n$. The small values for enthalpies of fusion result because the orientation disorder normally present only in the liquid state was already present in the solid. Similarly, Timmermans[26] has identified a class of orientationally disordered solids composed of rigid, compact molecules of approximately spherical shape (globular molecules) and with entropies of fusion below 20 J/mol$^{-1}$K$^{-1}$. Since many of these orientationally disordered solids flow under stress they have also been called plastic crystals. The term "premelting" has been used to describe the change associated with the transition to the orientationally disordered phase. These properties are often found for the high-temperature phases of salts with highly symmetric ions. The high-temperature phases of $NaClO_4$ (Ref. 27), $KClO_4$ (Ref. 28), $NaNO_3$ (Refs. 11,22), and $KNO_3$ (Refs. 11,22) have been identified as orientationally disordered crystals.

On the basis of the estimated enthalpies and entropies of transition it would appear that the high-temperature phase of $Cs_2CdCl_4$ is orientationally disordered. The discrete tetrahedral $CdCl_4^{2-}$ ion sits in the cavity created by the $Cs^+$ ions in a structure that in certain ways resembles the room-temperature $K_2SO_4$ but without apparent order in the orientation of the Cd-Cl bond direction. The molecules are not free to rotate but rapidly interchange among several distinguishable but energetically equivalent positions.

The fact that the Raman bands for the $CdCl_4^{2-}$ are relatively broad together with the high intensity and lack of structure in the Rayleigh wing (Figs. 2, 4, and 5) further suggests disorder of the tetrahedron. In ordered solids which contain polyatomic ions, the relative center-of-mass motions of whole ions give rise to modes of vibration called external modes which are often separated by a band gap from the internal modes associated with the vibrations of the polyatomic ions. No bands due to external modes of the $Cs^+$ or the $CdCl_4^{2-}$ were detected in the 30 to 100 $cm^{-1}$ region although a total of 24 external modes are Raman active for the $K_2SO_4$ structure.[15] Failure to observe external modes could be due to two factors. Since both the $Cs^+$ and $CdCl_4^{2-}$ ions are spherically symmetric the polarizability derivatives $(\delta\alpha/\delta Q)$ associated with the external modes of vibration are expected to be small and give rise to low-intensity bands. Appreciable disorder in the structure will cause the external modes to broaden and overlap with the result that no band structure can be resolved and the Raman intensity associated with the external models will appear generally as increased intensity of the Rayleigh wing. The increase in the intensity in the $I(\omega)$ spectra (Figs. 2, 4, and 5) in the Rayleigh wing region that accompanies the increase in temperature can be attributed in part to the temperature-dependent term in the equation to describe the Raman intensity [Refs. 12, 13, and Eq. (1)]. Density fluctuations within the crystal can also cause an increase in the Rayleigh scattering (centered at 0 $cm^{-1}$) and result in an increase in the Rayleigh wing intensity.[23] A detailed study of the Rayleigh scattering can be difficult because of the serious problem from reflected light at zero frequency. The fact that spectra presented in the $R_Q(\omega)$ format (Fig. 3) were essentially temperature independent in the 30 to 100 $cm^{-1}$ region indicated that the $I(\omega)$ spectra were properly normalized by the Bose-Einstein term in Eq. (1). No discrete bands were detected in the 30 to 100 $cm^{-1}$ region of the spectrum in the $R_Q(\omega)$ that could be assigned to external modes of the high-temperature form of $Cs_2\,CdCl_4$. There was no evidence to suggest that the high-temperature phase was ordered.

It is interesting to note that local order increased around the cadmium ion in the transition from the low-temperature to the high-temperature phase although the measured overall entropy increased. The frequency of the Cd-Cl stretching vibration increased from 196 to 268 $cm^{-1}$ when the coordination changed from octahedral to tetrahedral, which implies that the bond strength is greater and the bond length is shorter for the Cd-Cl bond in the tetrahedral coordination. In addition, the half-width of the band at 196 $cm^{-1}$ (37 $cm^{-1}$) was much greater than the half-width of the band at 268 $cm^{-1}$ (29 $cm^{-1}$). Since the half width of a band may be inversely related to the range of environments and thermal amplitudes of vibration it can be concluded that there is a greater distribution of bond lengths for the octahedrally coordinated cadmium. Nevertheless, the overall order of the crystal decreased because of the change in the $Cs^+$ sublattice and the orientational disorder of the $CdCl_4^{2-}$ ion.

## CONCLUSION

Raman spectra for $Cs_2CdCl_4$ measured for samples over a wide range of temperatures from the room-temperature solid to the molten salt revealed the presence of an unusual second-order-like phase transition. The transition occurred over a 25 °C temperature interval from 435 to 460 °C and between these temperatures the characteristic Raman bands associated with both the high-temperature phase and the low-temperature phase were observed simultaneously. The transition was associated with the rearrangement of the coordination about the cadmium ion from an array-type octahedron at low temperature to a discrete tetrahedral $CdCl_4^{2-}$ polyatomic ion at high temperature. The two coordinations of cadmium coexisted in dynamic equilibrium. Measurement of the entropy of the coordination change indicated that the high-temperature phase was orientationally disordered.

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has now been reassigned to the formation of $Cs_3CdCl_5$. In pure $Cs_2CdCl_4$, the presence of the band at 268 $cm^{-1}$ due to $CdCl_4{}^{2-}$ was not detected until 435 °C.

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