PHYSICAL REVIEW B VOLUME 30, NUMBER 10 15 NOVEMBER 1984

Specific heat and thermal-conductivity measurements on cesium and thallous halide crystals at low temperatures

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(Received 28 December 1983; revised manuscript received 12 July 1984)

Specific-heat and thermal-conductivity measurements in the temperature range of 1.7 to 20 K are reported on single crystals of CsBr, CsI, TlBr, and TlCl and on a polycrystalline sample of TlI. All crystals display minima in the effective Debye temperatures which are reflected in maxima in C/T^3-versus-T curves, and these extrema are especially pronounced for TlCl. Comparisons are made with the predictions of existing lattice-dynamics calculations, and the specific heat of TlBr is in very good agreement with the shell-model calculations of Cowley and Okazaki. A Schottky specific-heat term is resolved in the cesium halides at the lowest temperatures and attributed to hydroxyl ions; by adopting the zero-field splitting for OH^- in KCl, hydroxyl concentrations $\sim 10^{20}$ cm^{-3} are estimated in CsBr and CsI. The C/T^3 maxima are fitted with Einstein terms added to the Debye backgrounds, and these fittings (together with the Schottky fits for CsBr and CsI) yield the following Debye temperatures: CsBr, 145 K; CsI, 124K; TlBr, 116 K; TlCl, 120 K; and TlI, 103 K. Thermal-conductivity data for all crystals display maxima at $\sim$4–5 K and an apparent T^3 boundary-scattering regime at the lowest temperatures. Phonon mean free paths at the higher temperatures are analyzed according to the Peierls relation, and for CsBr and TlCl it is found that the Debye modes are the dominant heat carriers. For the remaining crystals, the Einstein modes also carry heat. (The Einstein modes at these higher temperatures dominate the specific heats, contributing up to 75% in the case of TlCl.) Thermal-conductivity measurements were also made on thin crystals ($\sim$0.05 cm) of CsBr, TlBr, and TlCl to examine the boundary-scattering region. It is found that in this region the limiting phonon mean free path for CsBr scales with the crystal dimension, and it is suggested that the suppression of the thermal conductivity may be due to the hydroxyl concentration. For TlBr and TlCl, the limiting phonon mean free path is $\sim$0.01 cm and is independent of the crystal thickness; this behavior is attributed to a mosaic structure within these crystals.

I. INTRODUCTION

Alkali halides are representative ionic crystals with simple-cubic structures and relatively simple interatomic potentials, and as such have been the subject of a great deal of experimental and theoretical work. It has been natural to concentrate on the NaCl-structure crystals, and, by comparison, the CsCl-type halides have been relatively unexplored from an experimental (and, to a lesser extent, from a theoretical) viewpoint.

There are significant structure-sensitive differences in some of the properties of the NaCl- and CsCl-type crystals. For example, the Grüneisen parameters for the cesium halides are practically temperature independent down to low temperatures,[1] whereas the NaCl-type crystals display a marked temperature dependence of this parameter. In the thallous halides, the elastic anisotropy, $2C_{44}/(C_{11}-C_{12})$, has a negative temperature dependence,[2] in contrast to the NaCl-type crystals. Other differences have been reported in the temperature and pressure dependences of the dielectric constants[3] and in thermal-expansion coefficients.[4]

The dielectric properties of the thallous halides are especially unique in that the dielectric constants are large ($\sim$30) and follow a Curie-Weiss law below room temperature,[5] suggestive of a dominant soft-optic mode. However, Samara[6] has shown from pressure and temperature measurements of the dielectric constants that the explicit temperature dependence of the polarizability is responsible for the Curie-Weiss behavior, rather than a soft mode. Subsequent neutron-scattering and infrared measurements on TlBr confirmed the absence of a dominant soft mode.[7]

The lattice dynamics of several CsCl-type crystals have been calculated based on various models (shell model, rigid-ion model, etc.).[8] These calculations predict the temperature dependence of the Debye temperature (Θ_D) at low temperatures, and two central results are obtained: (1) Θ_D at $T\to 0$ for comparison with Θ_D from elastic constant measurements, and (2) the position of a minimum in Θ_D in the helium-temperature range. The former property is not very model dependent because $\Theta_D(0)$ is determined primarily from the elastic continuum. On the other hand, the position and depth of the minimum in Θ_D results from the first rapid rise in the density of states (i.e., above the $\omega \propto k^2$ Debye background) and so is very model dependent. However, there do not appear to be adequate specific-heat data in the literature for the CsCl-type crystals in the neighborhood of these predicted minima in the Θ_D's. In addition, no measurements of the thermal conductivities of CsCl-type crystals at low temperatures have been reported.

The purpose of the studies here was to measure the specific heats and thermal conductivities of several CsCl-type crystals at low temperatures, namely TlBr, TlCl, TlI, CsBr, and CsI. There were several motivations for these measurements: (1) to provide specific-heat data for comparisons with theoretical predictions, (2) to investigate the nature of heat conduction in these crystals, and (3) to gain a better understanding of these materials, because, owing to their unusual thermal properties, they are becoming technologically important for enthalpy stabilization in superconducting windings.[9]

Large single crystals of CsBr, CsI, TlBr, and TlCl of optical quality are available commercially. TlI can be grown in the CsCl structure at elevated temperatures, but upon cooling transforms to a polycrystalline mass at 170 °C with a double-layered orthorhombic structure (D_{2h}^{17}-*Cmcm*).[10] Similarly, CsCl can be grown in the CsCl structure, but at 450 °C transforms to a mechanically unstable NaCl structure. Finally, CsF and TlF are difficult to study experimentally as they are both extremely hygroscopic and the latter fluoride is hazardous.

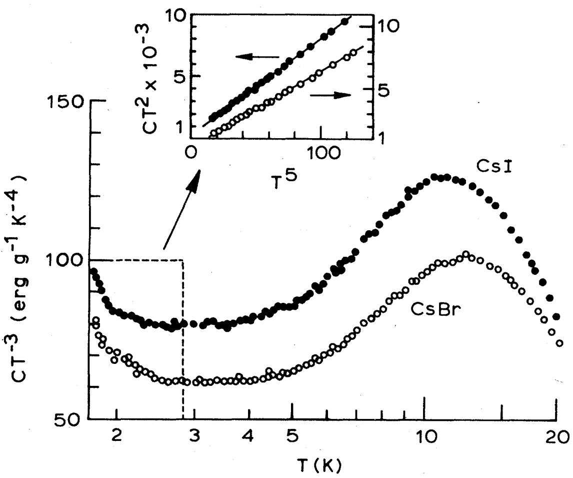

FIG. 1. Specific heats of CsBr and CsI plotted as C/T^3 vs T. Both crystals display maxima in C/T^3 at about 12 K and a sharp rise in C/T^3 below 3 K. The latter features follow a Schottky term as shown in the inset and are believed due to hydroxyl impurities.

II. EXPERIMENTAL METHODS AND RESULTS

Single crystals of CsBr, CsI, TlBr, and TlCl of good optical quality were obtained from Harshaw Chemical Co. (Solon, Ohio), and the typical impurity levels (e.g., Fe, Na, etc.) are reported to be <0.1 ppm.[11] A polycrystalline sample of TlI was also obtained from Harshaw. Some specific-heat data on these thallous halides were previously measured[12] on crystals of comparable quality (see below).

Specific-heat measurements here were performed by a pulse method in the adiabatic calorimeter described elsewhere.[12] Briefly, the addenda were kept to a minimum by fixturing the heater ($\sim 200\ \Omega$) and a carbon-chip thermometer (~ 10 mg) directly on the sample, and the $\Delta T/T$ values were maintained at $\simeq 2\%$. The addenda contribution to the specific heat is largest at the lowest temperature (1.7 K), and in the measurements here this maximum addenda contribution varied from 4.2% for TlBr to 9.2% for TlI. Owing to the small addenda corrections, the uncertainty in the method is believed to be less than $\pm 5\%$.

Thermal-conductivity measurements were made on bars cut from the crystals (and on thin sections; see below). All cutting operations were done slowly under oil using a thin diamond saw, and all cut samples were annealed in Grafoil for 24 h at 350 °C or 450 °C for the thallous and cesium halides, respectively. No effort was made to polish the cut surfaces which appeared smooth.

Owing to the large thermal conductivities of these crystals, the "two-heater, one-thermometer" linear-heat-flow method was used.[13] The primary advantage of this method is that only one thermometer calibration is required, since, for these crystals, the ΔT values tend to be relatively small. The main uncertainty in the method stems from measuring the separation of the heaters ($\lesssim \pm 5\%$).

The thermal conductivities of thin (~ 0.5-mm) bars were also measured, and samples were assembled by loading 25–30 bars (or fibers; see below) into a thin-walled plastic straw (3.2 mm diam) for mechanical support. Actually, sections of a straw were used to allow gaps for winding the two heaters, and a tight-packing arrangement was obtained to ensure efficient transverse heating at the heater locations. The free end of the bundle of bars was potted with silver epoxy through which several thin copper wires were threaded; these wires, in turn, were wrapped around, and varnished to, a carbon-chip thermometer. In all the thermal-conductivity measurements here, the overall A/l ratios were ~ 0.1–0.2 cm, and these measurements were also made in the adiabatic calorimeter mentioned above.

Specific-heat data, 1.7–20 K, on the cesium and thallous halides are shown in Figs. 1 and 2, respectively. The data are plotted as C/T^3 to illustrate the departure from

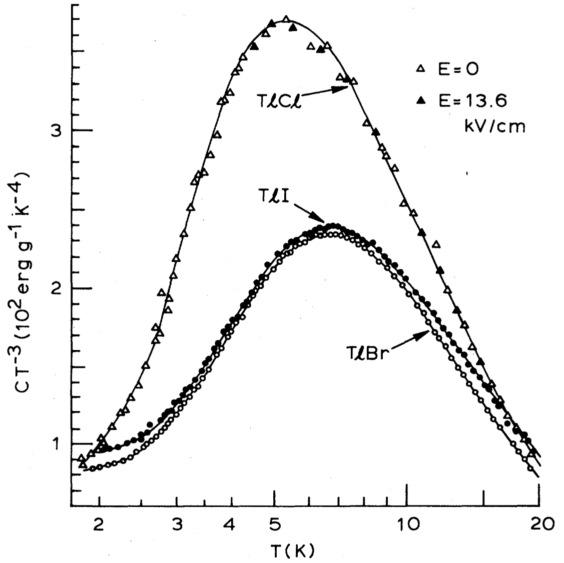

FIG. 2. Specific heats of the thallous halides plotted as C/T^3 vs T. All crystals display pronounced maxima in C/T^3 at 5–7 K, especially TlCl. The electric field dependence of the specific heat of TlCl is shown in the neighborhood of the maximum in C/T^3.

Debye behavior. For the cesium halides in Fig. 1, an additional excitation contributes to the specific heat below about 3 K, and the inset of Fig. 1 indicates that this excitation follows a Schottky term very well (see below).

The data in Fig. 2 for the thallous halides include the data reported previously.[12] There are two major additions in Fig. 2 compared to the previously reported data: (1) data are extended in Fig. 2 down to 1.7 K, and (2) data for TlCl are shown measured with an applied electric field of 13.6 kV/cm.

The reason for extending the thallous halide measurements to 1.7 K was to look for an additional excitation, as occurs in the cesium halides (Fig. 1). The reason for the electric field measurements was as follows: The C/T^3 maximum for TlCl in Fig. 2 represents such a dominating effect (the Debye contribution to this maximum is only 25%; see below) and the depth of the minimum in the effective Θ_D for TlCl (76 K, Fig. 3) disagrees so substantially with lattice-dynamics calculations (127 K; see below), that it was logical to question whether some portion of this C/T^3 maximum may be due either to a polar impurity or to an optic mode that becomes low lying in the helium-temperature range (note that neutron-scattering data[7] on TlBr were not measured below 100 K). In either case, an E field is expected to alter the specific heat.[14] However, as seen in Fig. 2, the applied electric field does not affect the position or height of the maximum in C/T^3 of TlCl,[15] and we conclude that this is an intrinsic effect.

The effective Debye temperatures of the cesium and thallous halides are derivable directly from the (smoothed) specific-heat data in Figs. 1 and 2 using published tables for the Debye function,[16] and these $\Theta_D - T$ data are shown in Fig. 3. Here, and throughout this paper, the reported Debye temperatures are normalized to one atom per formula weight. In arriving at these data in Fig. 3 the specific-heat data for the cesium halides below 3 K have been deleted due to the Schottky-type excitation (Fig. 1). The Θ_D intercept values at $T=0$ in Fig. 3 result from the data fittings discussed below. As seen, Θ_D for TlCl displays the deepest minimum (from 120 K at $T=0$ to 76 K at 5.4 K) of all the halides measured.

Thermal-conductivity data measured on bars [($\sim 0.15 \times 1.0$)-cm^2 cross section] of the cesium and thallous halides are shown in Figs. 4 and 5, respectively. For all materials, the thermal conductivity (K) passes through a maximum, and, at the lowest temperatures, a $K \propto T^3$ boundary-scattering limit is apparently reached. Some data from separate runs on TlBr and TlCl are also shown in Fig. 5.

Although the crystals in Figs. 4 and 5 have relatively large maximum K values (2–7 W cm^{-1}K^{-1}), it is surprising that the TlBr and TlCl crystals do not have much *larger* thermal conductivities because the specific heats and densities of these crystals are very large (Fig. 2). That is, if we adopt the kinetic expression,

$$K = \tfrac{1}{3} C \rho \bar{v} \lambda \ , \qquad (1)$$

where ρ is the density, $\bar{v}$ is the average sound velocity, and λ is the phonon mean free path, then in the boundary-scattering limit, $\lambda \simeq d$, where d is the minimum crystal thickness. For TlBr and TlCl, $\rho = 7.557$ and 7.000 g/cm^3, respectively, and Morse and Lawson[2] report $\bar{v} = 1.82 \times 10^5$

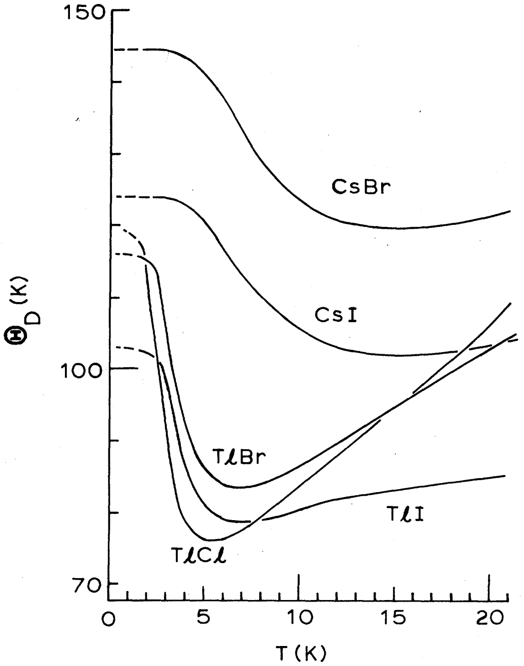

FIG. 3. Temperature dependences of the effective Debye temperatures of the cesium and thallous halides derived from the data in Figs. 1 and 2. The Θ_D values shown at $T=0$ K result from the fittings described in the text.

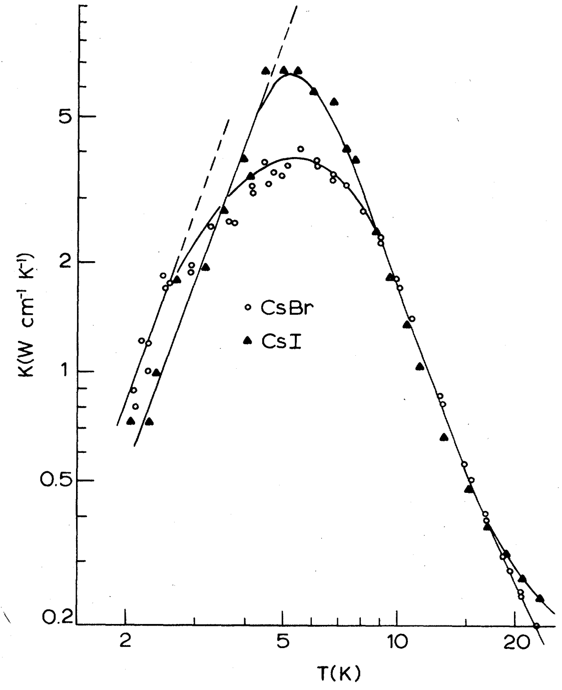

FIG. 4. Thermal-conductivity data measured on crystals of CsBr and CsI. The dashed lines represent the T^3 boundary-scattering regions.

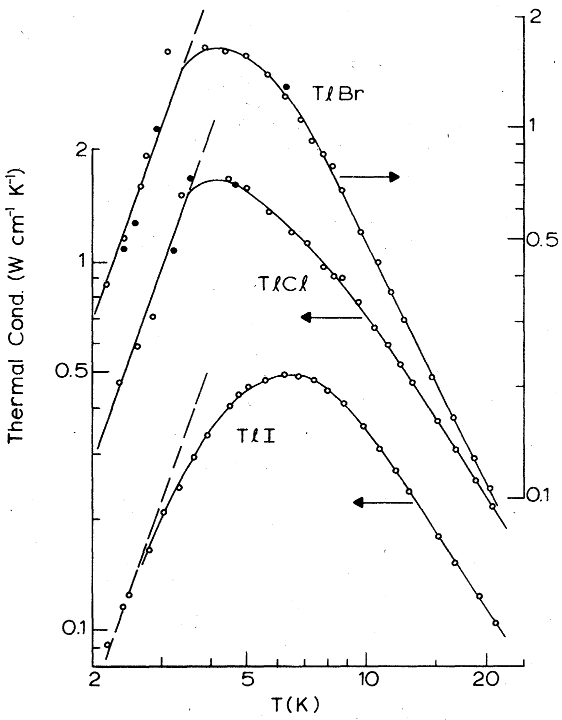

FIG. 5. Thermal-conductivity data measured on crystals of TlBr and TlCl, and on a polycrystalline sample of TlI. The dashed lines represent the T^3 boundary-scattering regions, and some duplicate data for TlBr and TlCl are shown (solid points).

cm/sec for TlBr. Using the C data in Fig. 2 for these crystals, Eq. (1) predicts that $K \sim 50$ W cm^{-1}K^{-1} for $d \sim 0.15$ cm near the maximum in K. Conversely, for CsBr and CsI ($\rho = 4.440$ and 4.526) the same exercise yields $K \sim 10$ W cm^{-1}K^{-1}, which agrees somewhat better with the measured data, Fig. 4.

The Casimir relation

$$K = 4.076 \times 10^{10} T^3 A^{1/2} / (\bar{v})^2$$

is useful for judging homogeneous boundary scattering, where A is the cross-sectional area of the bar and $\bar{v}$ is the average sound velocity. Applying this relation to the crystals here, we find that at 2 K the predicted thermal conductivities for the thallous halides are at least an order of magnitude *larger* than the measured values in Fig. 5. For the cesium halides the comparison is somewhat better, the predicted values being about 4 times larger than the experimental values at 2 K in Fig. 4. These results indicate that the scattering of phonons by defects is important in these crystals despite the very small impurity levels quoted above.

Phonon scattering in these CsCl-structure crystals was pursued further by measuring thermal conductivities on *thin* samples. Thin bars of TlCl (0.64×0.64 mm^2) and CsBr (0.64×0.64 mm^2) were cut from the crystals as described above, and thin fibers of TlBr (0.49 mm diam) were obtained from Harshaw (The CsI crystal proved too brittle to cut). The results of these measurements for CsBr, and for TlBr and TlCl, are shown in Figs. 6 and 7, respectively; also shown are the "bulk" thermal conductivities for these crystals from Figs. 4 and 5 for comparison.

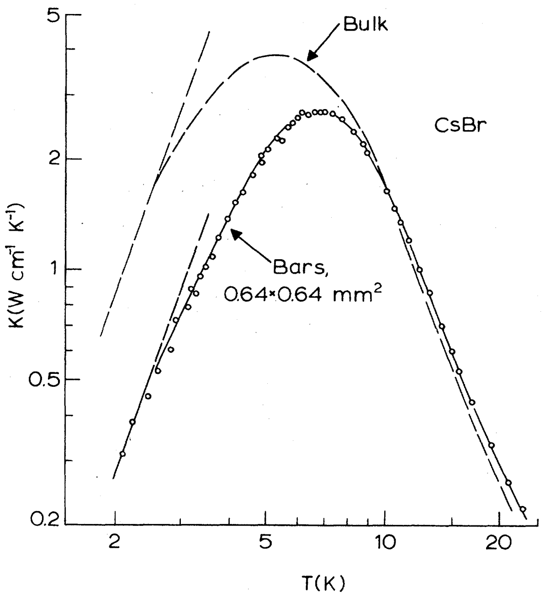

FIG. 6. Thermal-conductivity data measured on thin crystals of CsBr compared to the "bulk" data from Fig. 4.

The thin-crystal data in Figs. 6 and 7 also approach the $K \propto T^3$ limit at the lowest temperatures, but there is a striking difference between CsBr and the thallous halides: The T^3 limit is depressed for CsBr, whereas this limit is

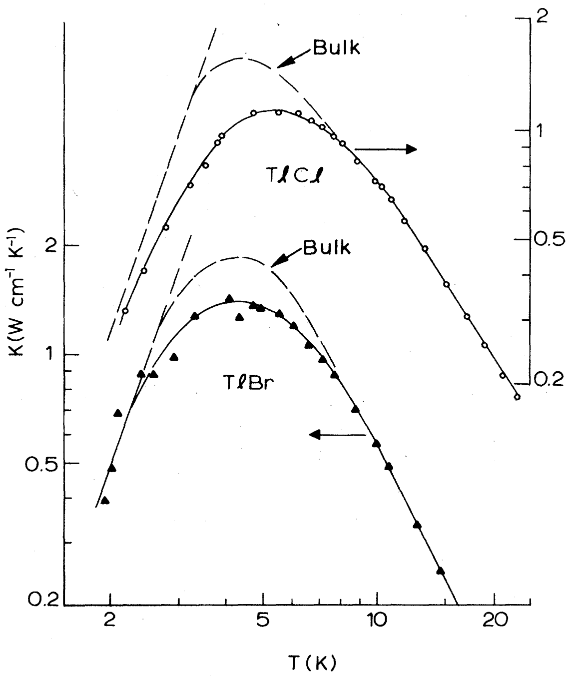

FIG. 7. Thermal-conductivity data measured on thin crystals ($\sim$0.05 cm) of TlBr and TlCl compared to the "bulk" data from Fig. 5. In contrast to CsBr (Fig. 6), the thick- and thin-sample data for these thallous halides approach the same limiting values in the T^3 boundary-scattering regions.

approximately the *same* for thick and thin crystals of the thallous halides. At the higher temperatures, the thick- and thin-sample thermal-conductivity data converge for all three crystals.

III. DATA ANALYSES

The thermal data above reveal significant differences between the cesium and thallous halides: The effective Debye temperatures for the cesium salts are larger than those for the thallous salts, and go through broad minima compared to the deep and narrow minima for the thallous salts. The scattering of phonons in CsBr appears to scale approximately with the crystal thickness, but the scattering in TlBr and TlCl appears to be independent of the crystal thickness. In this section we will pursue analyses of these thermal data according to simple models.

The specific-heat data for the cesium halides in Fig. 1 show that an excitation makes a significant contribution to C/T^3 below about 3 K. Attempts were made to fit these data to various specific-heat functionals, and excellent fits were obtained with the high-temperature form of the Schottky term, $C_{\text{Sch}} \propto T^{-2}$, added to a T^3 Debye background. These CT^2-versus-T^5 fits are shown in the inset of Fig. 1. Debye temperatures for CsBr and CsI are obtained from the slopes of these fits, and are 146.0 and 125.1 K, respectively.

The general, multilevel Schottky term has a T^{-2} dependence at temperatures larger than the level splitting, so the presence of this term says nothing about the responsible excitation. An impurity effect is suggested, which, however, is *absent* in the thallous halides. Since the cesium halides are far more hygroscopic than the thallous halides, this Schottky term may be due to hydroxyl ions. It is known that OH^- ions occupy halogen sites in NaCl-type crystals (e.g., KCl and KBr) and have six equilibrium orientations along [100].[17] The ground state is tunneling-split into a singlet A_{1u} of energy -2δ, a triplet T_{1g} of zero energy, and a doublet E_q of energy δ, where δ is the zero-field splitting.[18] The Schottky contribution to the specific heat from these tunneling states is[19]

$$C_{\text{Sch}} = \frac{6Nky^2(2e^{-2y}+3e^{-3y}+e^{-5y})}{(1+3e^{-2y}+2e^{-3y})^2}, \quad y=\delta/T \qquad (2)$$

where N is the OH^- concentration in cm^{-3}. At $T \gg \delta$, Eq. (2) reduces to $C_{\text{Sch}} = Nk(\delta/T)^2$. Assuming this form applies to the CsCl structure and using the fitted data for CsBr and CsI, we find that $N\delta^2 = 1.13\times10^{19}$ and 9.68×10^{18} $\text{K}^2\,\text{cm}^{-3}$, respectively. In the NaCl-type crystals, $\delta \simeq 0.34$ K,[20] which implies OH^- concentrations in these cesium halide crystals of $N \simeq 10^{20}$ cm^{-3}. These concentrations are comparable to those found in KCl crystals,[18] but apparently were not detected in the chemical analyses for Fe, Na, etc. in these cesium salts. (An alternate suggestion[11] is the CN^- ion; however, the splitting for this ion is so small, $\delta \simeq 0.07$ K,[21] that unrealistically large concentrations, $N \sim 2\times10^{21}$ cm^{-3}, are needed to satisfy the fitting parameters.)

Phonon scattering by the (suspected) hydroxyl ions in the cesium halides would be most pronounced at temperatures near the zero-field splitting ($\sim$0.3 K), and this may prove to be a useful area for future research. We can speculate here that the hydroxyl impurities may be responsible for the depressed thermal conductivities of these cesium salts in the T^3 limit, as discussed above.

The specific-heat data in Figs. 1 and 2 show large maxima in C/T^3, and it has been found[12] that such maxima can often be described very accurately by a single Einstein-oscillator term added to the Debye background,

$$C = 3nRD(T/\Theta_D) + 3Rrx^2e^x/(e^x-1)^2, \quad x = \Theta_E/T \qquad (3)$$

where n is the number of atoms per formula weight, $D(\Theta_D/T)$ and Θ_D are the Debye function and temperature, respectively, r is the number of Einstein oscillators per formula weight, and Θ_E is the Einstein temperature. In the general case, if one has knowledge of optical modes and if such modes are approximately independent of the wave vector, then these modes can be represented by appropriate Einstein terms.[22] In our case here, the Einstein term can be thought of as representing the first rapid rise in the density of states above the Debye background, and the analyses according to Eq. (3) have the particular advantage of yielding the Debye temperatures.

The specific-heat data for the cesium and thallous halides were fitted to Eq. (3) using a three-level-fitting regime (i.e., for Θ_D, Θ_E, and r) which incorporated a table of the Debye function.[16] The cesium halide data below 4 K were not used in these fits to avoid the tail of the Schottky term (Fig. 1). These fitted data are shown in Fig. 8 for the cesium halides. In these plots, C_{ex} is the excess specific heat, $C_{\text{ex}} = C_{\text{exp}} - C_{\text{Debye}}$, and excellent fits to the data are obtained over several orders of magnitude in $T^2C_{\text{ex}}/3R$ [the slight curvature in Fig. 8 is due to the

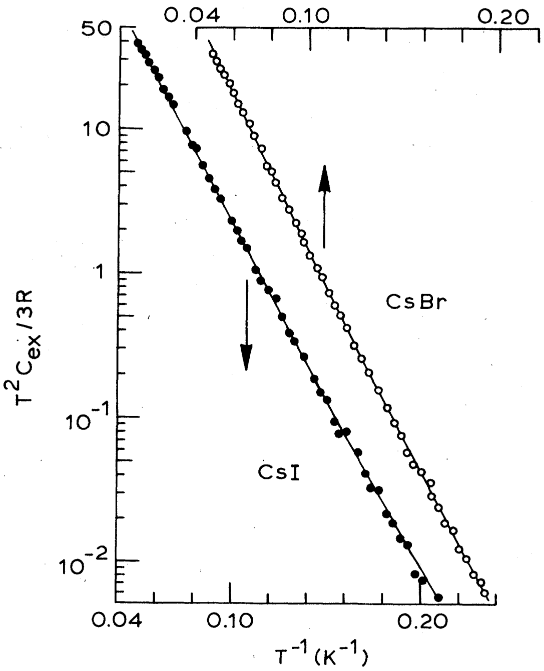

FIG. 8. Fittings of the CsBr and CsI specific-heat data to the single Einstein-oscillator model, Eq. (3). Data below 4 K were not included in these fittings to avoid the tail of the Schottky term, Fig. 1.

TABLE I. Fitting parameters, Eq. (3).

Crystal	Θ_D (K)	Θ_E (K)	ω_E (cm^{-1})	r	N_E/N_D
TlCl	120.4	26.14	18.17	0.239	23.31
TlBr	115.7	31.34	21.78	0.251	12.64
TlI	103.2	33.97	23.61	0.353	9.89
CsBr	143.2	60.09	41.76	0.331	4.49
CsI	122.7	56.36	39.17	0.397	4.10

$T \ll \Theta_E$ form of Eq. (3) used for plotting]. Similar fits for limited data on the thallous halides were reported previously;[12] the fits obtained here are equivalent, and only the fitting parameters are reported (Table I). The correlation coefficients for these fits were $\simeq$99.6% and the fitting parameters are given in Table I. Also given in Table I is an approximate estimate of the ratio of the number of Einstein modes (N_E) to Debye modes (N_D) excited at the Einstein temperature,[23]

$$N_E/N_D \simeq r(\Theta_D/\Theta_E)^3 \; . \tag{4}$$

The Debye contribution to the specific heat of these crystals can be estimated directly from the Debye temperatures in Table I and compared to the experimental data. At the maximum in C/T^3 it is found that the Debye contribution varies from 25% for TlCl to 64% for CsI. Thus, the Einstein modes *dominate* the specific heats of these halides, particularly so in the case of the thallous halides, and this is also seen in the N_E/N_D values in Table I. A similar dominance has been found in the hexagonal tungsten bronzes[23] and in ferroelectrics.[12]

The agreement between the Debye temperatures for the cesium halides from the Schottky and Einstein fits is quite good: CsBr, $(144.6\pm0.97\%)K$; CsI, $(123.9 \pm 0.97\%)K$. These uncertainties in the Debye temperatures translate into uncertainties in C/T^3 of $\pm$2.9%, which is commensurate with the experimental inaccuracy. Furthermore, the fitting parameters demonstrate that the Schottky term makes a negligible contribution in the fitting temperature range of the Einstein term, and vice versa.

It has recently been pointed out by Pederson and Brewer[24] that a linear relationship exists between Θ_D and the reduced mass (μ) for cubic crystals, and this relation holds very well for the halides in Table I. Going further, the Einstein frequencies ω_E scale with $\mu^{-1/2}$ for the cesium halides; for the thallous halides, the ω_E values in Table I do not scale with $\mu^{-1/2}$, but tend to increase as the mass of the halogen ion increases.

Turning next to the thermal-conductivity data, the primary question is what are the heat-carrying modes in these crystals? This question deserves special consideration since, as seen above, the Einstein term *dominates* the specific heat in these halides at low temperatures. One approach to this problem of determining the heat-carrying phonons is to employ the well-known result due to Peierls,[25]

$$\lambda = \lambda_\infty e^{\Theta_D/2T} \; , \tag{5}$$

for the phonon mean free path, which has been verified in several dielectric crystals. This relation pertains to the temperature region well above the maximum in the thermal conductivity and has been derived on the assumption that the Debye phonons are the dominant heat carriers. What is important here is that if $\lambda \propto K/C_D$ [i.e., from Eq. (1)] follows Eq. (5), at these higher temperatures, where C_D is the Debye contribution to the specific heat, and if there is internal consistency between the Θ_D's from Eq. (5) and from Table I, then it can reasonably be concluded that the Debye phonons carry heat and the Einstein modes do not.

Consequently, plots of $\ln\lambda$ versus T^{-1} were constructed from the experimental data using Eq. (1) in two ways: (1) using the experimental specific-heat data (i.e., Debye plus Einstein contributions), and (2) using only the Debye contribution to the specific heat *via* the Debye temperatures in Table I. In constructing these plots, the data for ρ and $\bar{v}$ quoted above were used, but we note that these data do

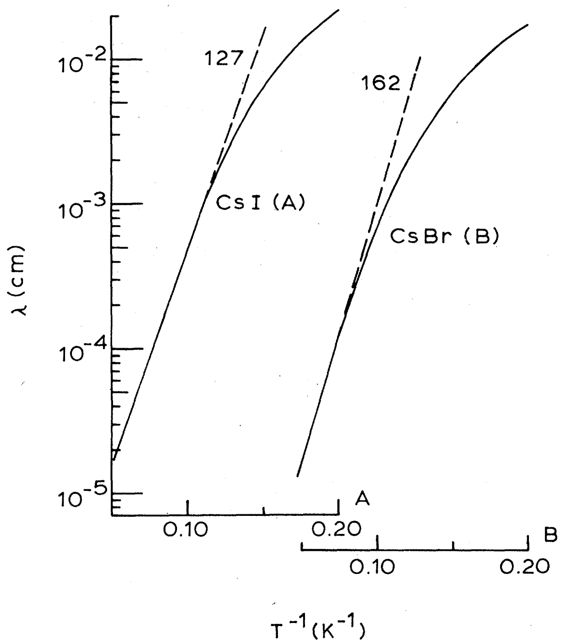

FIG. 9. Plots of the temperature dependence of the phonon mean free paths in CsBr and CsI. These plots were constructed using Eq. (1) and the thermal-conductivity data from Fig. 4 (and from Fig. 6 in the overlap region) and specific-heat data from Fig. 1. Similar plots were constructed using just the Debye specific-heat data obtained from the Θ_D's in Table I. According to the Peierls relation, Eq. (5), the slopes of the linear portions of these curves are simply related to Θ_D, and the dashed curves correspond to the Θ_D values shown. Note that the Θ_D value shown for CsI agrees well with the calorimetric value, Table II (also see text).

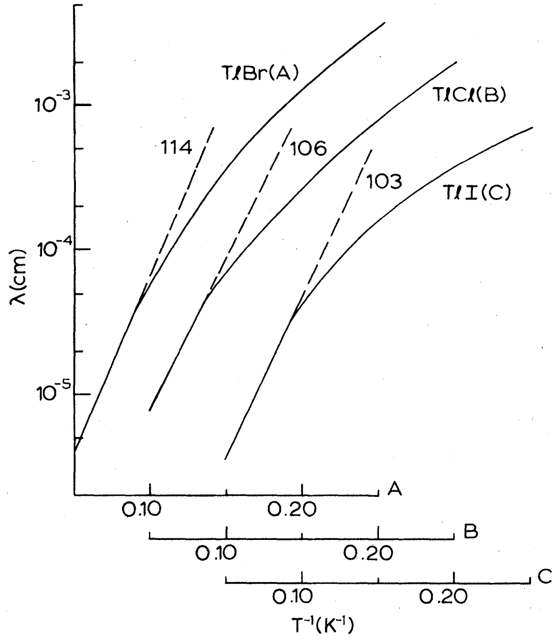

FIG. 10. Phonon mean-free-path data for the thallous halides, analogous to the Fig. 10 plot for the cesium halides. Note that the Θ_D values shown for TlBr and TlI agree well with the calorimetric values in Table II.

not affect the Θ_D values according to Eq. (5). Thermal-conductivity data at the higher temperatures on both thick and thin crystals (Figs. 6 and 7) were used, and examples of these λ plots are shown in Figs. 9 and 10 for the cesium and thallous halide crystals, respectively. For these plots, the Debye plus Einstein specific heats were used, and at the higher temperatures, well removed from the $K \propto T^3$ region, a linear lnλ versus T^{-1} region is reached from which Θ_D can be determined according to Eq. (5). The results of these linear-region fittings are summarized in Table II.

The Table II data reveal some interesting contrasts: (1) For TlCl and CsBr, there is excellent agreement with the calorimetric Θ_D's if the Einstein modes are assumed *not* to carry heat, whereas (2) for TlBr, TlI, and CsI, the excellent agreement between the Θ_D's suggests that the Einstein modes do carry heat in these crystals. The latter agreement is probably fortuitous since, if non-Debye modes carry heat, the basic assumptions leading to Eq. (5) are violated. We remark in this regard, however, that the Einstein terms make such a large contribution in the temperature ranges involved here that the analyses are very sensitive to whether the D or $D+E$ contributions are used in Eq. (1).

TABLE II. Debye temperatures from mean-free-path fits.

Crystal	Θ_D (calorimetric)[a] (K)	$\Theta_D(D)$[b] (K)	$\Theta_D(D+E)$[b] (K)
TlBr	116	135	114
TlCl	120	120	106
TlI	103	123	103
CsBr	145	148	162
CsI	124	144	127

[a] Average Θ_D's from Schottky and Einstein fits to cesium halide data.

[b] D, Debye specific heat only used in Eq. (1); $D+E$, experimental specific heat used in Eq. (1).

TABLE III. Boundary-scattering mean free paths.

Crystal	Minimum crystal thickness (cm)	λ_c (cm)
TlBr	0.145	0.016
TlBr	0.049	0.016
TlCl	0.155	0.0084
TlCl	0.064	0.0077
TlI[a]	0.169	0.0020
CsBr	0.172	0.063
CsBr	0.064	0.020
CsI	0.156	0.032

[a] Fused polycrystalline sample.

Returning to the apparent boundary-scattering regions seen in the thermal conductivities at the lowest temperatures in Figs. 4–7, we shall employ Eq. (1) to find λ_c, the limiting phonon mean free path in these crystals. The heat-carrying modes identified above are assumed to be correct, and the appropriate specific heats are used in Eq. (1). The average sound velocity $\bar{v}$ quoted above for TlBr will be used for all crystals (see below), and the Schottky term in the specific heat of the cesium halides is assumed to be localized (i.e., this excitation does not carry heat). Using smoothed thermal-conductivity data in the boundary-scattering range, λ_c data were determined, and these data are given in Table III compared to the crystal thicknesses. The Table III data demonstrate a marked contrast between the cesium and thallous halides: For CsBr, the limiting phonon mean free path $\lambda_c \simeq d/3$, where d is the crystal thickness, whereas for TlBr and TlCl, $\lambda_c \simeq 0.016$–0.008 cm, respectively, independent of d.

IV. DISCUSSION

In the above section, specific-heat data at constant pressure have been analyzed, whereas data at constant volume are more suitable for comparisons with theories. This correction involves the thermal-expansion coefficient and the adiabatic compressibility, and estimates of this correction by Sorai[26] show that it is smaller than the experimental inaccuracy; hence, it has been ignored here.

A. Cesium halides

Specific-heat data on CsBr and CsI below room temperature have been reported by several authors over the following temperature ranges. For CsBr: 20–300,[27] 1.14–5.62,[28] and 3–9 K.[29] For CsI: 2.1–10 K (Ref. 30) and 30–100 K (Ref. 31). Where possible, comparisons with the experimental data reported here are very good. However, as alluded to previously, none of these reported data sets spans the temperature range where the minimum in Θ_D is pronounced.

Some of the above measurements on CsBr and CsI extend to temperatures[28,30] sufficiently low where the

Schottky term reported here would make a noticeable contribution, and the crystals measured are reportedly the same quality Harshaw crystals measured here. These authors (Refs. 28–30) did not report this Schottky term; on the other hand, they did not look for it. In fact, it is apparent in these other data that C/T^3 increases with decreasing temperature at the lowest temperatures, as in Fig. 1, but analyses of these data were not pursued.

The Debye temperatures for CsBr (145 K) and CsI (124 K) reported above from the Schottky and Einstein fittings are in good agreement with the Θ_D's at $T\rightarrow0$ K reported from other calorimetric studies and from elastic constant measurements. From the former measurements, Θ_D values of 150.9 K (Ref. 28) and 127.7 K (Ref. 30) have been reported for CsBr and CsI, respectively. From elastic constant data, Θ_D's for CsBr of 149.0 K (Ref. 32) and 148.8 K (Ref. 33) and for CsI of 129.4 K (Ref. 30) have been reported.

Turning to theoretical studies, Karo and Hardy[34] have published detailed calculations of the frequency distributions and dispersion curves for CsBr, CsCl, and CsI according to three models: the rigid-ion, polarization-dipole, and deformation-dipole models. These authors present curves of the predicted temperature dependence of the effective Debye temperature according to each model, and these data can be compared directly with the curves in Fig. 3. First, these lattice-dynamics calculations all locate the minima in the Θ_D's for CsBr and CsI at about 15 K, in good agreement with the experimental data. The depth of these minima increase upon going from the rigid-ion to the deformation-dipole to the polarization-dipole model, and for both CsBr and CsI the best agreement with experimental data results from the deformation-dipole model. For example, the predicted Θ_D minima are 120 and 107 K, compared to the Fig. 3 minima of 120 and 102 K for CsBr and CsI, respectively. From the limited data available to Karo and Hardy, they also concluded tentatively that the deformation-dipole model appeared to give the best representation of the cesium halides.

As mentioned above, the Einstein-oscillator model, Eq. (3), is a convenient representation of the maximum in C/T^3 above the Debye background, and can be thought of as reflecting the first rapid rise in the density of states. Accordingly, the Einstein frequencies ω_E in Table I might be expected to correspond to the calculated positions of the first Van Hove singularities in the frequency distributions from the lattice-dynamics models. For CsBr and CsI, Karo and Hardy[34] report these calculated positions at about 5 THz$\sim$170 cm^{-1}. However, from Table I the ω_E's for CsBr and CsI are smaller by a factor of 4. As will be seen below, the agreement for the thallous halides is much better.

B. Thallous halides

Turning next to the thallous halides, there have been fewer reported specific-heat measurements than for the cesium halides: Specific-heat data from 5 to 300 K have been reported for TlBr (Ref. 35) and for TlCl and TlI (Ref. 36); data for TlCl from 15 to 310 K have also been reported.[37] As with the cesium halides, complete specific-heat data in the neighborhood of the minima have not previously been published. The specific-heat data reported here agree well with published data, although the latter data are reported at such widely spaced temperature intervals that detailed comparisons are difficult.

With one exception, all of the experimentally determined Debye temperatures quoted in the literature for the thallous halides come from elastic constant measurements: For TlCl, both Haussühl[38] and Joshi *et al.*[39] report $\Theta_D=125$ K, which is in good agreement with the fitted value in Table I (120 K). For TlBr, elastic Debye temperatures of 132 K (Ref. 2) and 128 K (Ref. 40) have been reported, together with values of 115 K (Ref. 38) and 114 K (Ref. 39), which are in better agreement with the Table I value (116 K). From calorimetric measurements above 5 K, Brade and Yates[35] report $\Theta_D=128$ K for TlBr. For TlI, no quoted Debye temperatures appear in the literature.

Turning to lattice-dynamics treatments, Cowley and Okazaki[7] have reported a detailed study of TlBr wherein the normal modes of vibration were measured at 100 and 300 K using neutron-scattering methods and the results were fitted to various rigid-ion and shell models. According to a shell model which yielded the most satisfactory agreement with the neutron data, these authors derived a curve of the temperature dependence of the effective Debye temperature for TlBr. This predicted curve demonstrated a minimum in Θ_D at about 7 K of depth 87 K, in excellent agreement with the experimental data in Fig. 3. The model also yielded $\Theta_D=132$ K at $T\rightarrow0$ K, which is in reasonably good agreement with the value reported here. Of particular significance, Cowley and Okazaki report a first rapid rise in the density of states for TlBr at about 0.65 Thz $\approx$22 cm^{-1}, in excellent agreement with the Einstein frequency in Table I.

The phonon vibrational frequencies of TlCl have been calculated by Kamal and Mendiratta[41] using a shell model. These authors report a minimum in the effective Θ_D of about 127 K at 13 K, which is significantly different than the experimental values (Fig. 3) of 76 K at 5.4 K. However, this shell model predicts the first rapid rise in the density of states at about 6 THz$\approx$20 cm^{-1}, which agrees reasonably well with the ω_E for TlCl in Table I.

Finally, turning to the new thermal-conductivity data on these halide crystals, it has long been recognized that in dielectric crystals the critical phonon mean free path (λ_c above) rarely equals the actual sample dimension. Differences are commonly ascribed to specular versus diffuse phonon scattering at crystal boundaries, and scattering by dislocations has been extensively studied.[42] In the annealed, CsCl-type crystals measured here under identical conditions, the λ_c values for CsBr scale approximately uniformly with the crystal dimensions (Table III), whereas for TlCl and TlBr, the λ_c values are ostensibly crystal-dimension independent. It is admittedly true that the data in Table III are dependent on the assignment of heat-carrying modes, as discussed above, but for a given crystal these qualitative conclusions are independent of these mode assignments. It is also true that the average sound velocity[2] for TlBr has been used for all crystals in arriving at the Table III data; however, this assumption is believed to introduce a very small error, and, moreover, does not affect the conclusions regarding a particular crystal. For example, the elastic constant data for CsI (Ref. 30) indicate that $\bar{v}=1.92\times10^5$ cm/sec, a value within 5% of the value used above.

The picture that emerges for CsBr and CsI is that although boundary scattering is clearly indicated by the scaling of λ_c to the crystal dimension, the magnitude of the thermal conductivity is reduced by the hydroxyl content inferred from the Schottky term in the specific heat.

The independence of λ_c on crystal dimension for TlBr and TlCl may be due to the "mosaic" structure within these crystals. That is, the results of small-angle x-ray-diffraction studies have shown that, regardless of the care in growing these crystals, there always exists a mosaic structure such that a mosaic spread of about 0.2°–0.3° is found in these crystals regardless of composition.[11,43] Moreover, the physical dimension of these mosaics is reportedly $\simeq 0.01$ cm, a value which agrees well with the critical mean free paths for TlBr and TlCl in Table III.

V. CONCLUSIONS

A large amount of new thermal data for certain cesium and thallous halides between 1.7 and 20 K has been presented. Specific-heat data have been compared with existing lattice-dynamics models, where possible, and it is perhaps significant that only in the case of TlBr, where neutron-scattering data are available, is there satisfactory agreement between the experimental and predicted behavior of the effective Debye temperature. Fitted values of the Debye temperatures at $T\rightarrow 0$ K are presented, and these values compare favorably with literature values. Minima in the effective Debye temperature are reflected in maxima in C/T^3, and these maxima can be fitted very accurately with a single Einstein-oscillator term. For TlBr and TlCl, the resulting Einstein frequencies agree very well with the positions of the first Van Hove singularities in the density of states, as predicted by various lattice-dynamics models. For CsBr, the corresponding agreement is poor.

The specific-heat data reported here represent the first complete set of data, to our knowledge, measured on the cesium and thallous halides in the temperature range of the minima in the effective Debye temperatures, and it is hoped that these data may stimulate refinements of the lattice-dynamics models.

A Schottky term in the specific heats of CsBr and CsI at the lowest temperatures has been resolved and tentatively attributed to OH^- ions occupying halogen sites, by analogy with OH^- ions in NaCl-type crystals. Adopting the zero-field splitting for KCl:OH, the Schottky terms in these cesium halides yield hydroxyl-ion concentrations that are comparable to the concentrations found in NaCl-type crystals.

The thermal-conductivity data reported here for the cesium halides are understandable in a straightforward fashion: The heat-carrying modes are identified in a self-consistent fashion from analyses of the temperature dependence of the phonon mean free path using the specific-heat data, and in the apparent boundary-scattering region the limiting mean free path is about one-third of the crystal thickness. The magnitude of the thermal conductivity of the cesium salts at the lowest temperatures is alleged to be uniformly reduced by the hydroxyl content. The heat-carrying modes are similarly identified in the thallous halide crystals, but in the boundary-scattering region the limiting mean free path is determined by a mosaic structure within the crystals rather than the crystal dimensions. No evidence is found for appreciable hydroxyl contents in the thallous halides.

ACKNOWLEDGMENTS

Portions of this research were supported by the U. S. Air Force Office of Scientific Research. The author is grateful to C. F. Clark and R. W. Arenz for technical assistance, and to A. C. Anderson and G. A. Samara for helpful discussions.

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