$\frac{5}{2}$, although we have no theoretical explanation for this slope.

Among the alkali halides, LiF is anomalous in some of its properties compared with the other salts, but its F-band position follows the same Mollwo-Ivey relation. We have identified the V_3 band in LiF, and shown that its position also is consistent with the other alkali halides.

[†] Work supported by U. S. Atomic Energy Commission. Based on part of a Ph. D. thesis submitted by M. R. Mayhugh.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 8 15 OCTOBER 1970

Study of Lattice Resonance Modes through Specific-Heat Measurements: KCl:Tl and KCl:Br[†][*]

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(Received 15 June 1970)

The specific heat of KCl doped with 1-, 3-, and 5-mole% TlCl and of KCl-KBr mixed crystals has been measured between 1 and 30 °K. The frequency associated with the resonance mode, caused by the heavy impurity, was determined to be 51 ± 8 cm^{-1} (wave number) for KCl : Tl and 110 ± 10 cm^{-1} for KCl : Br, in close agreement with the resonance frequencies determined from thermal conductivity and infrared absorption. Our findings support the picture that the impurity modes in these cases are determined to a good approximation by the different mass of the impurity and not by a change in the local binding forces.

I. INTRODUCTION

The introduction of an impurity atom into an otherwise perfect crystal changes the vibrational spectrum of the pure crystal.[1,2] If, in particular, the impurity is heavy compared with the atoms of the host lattice, a new mode with a frequency within the normal phonon-frequency range appears. Much information about such resonance modes has been obtained from far-infrared spectroscopy[3] and thermal conductivity measurements.[4]

In this paper, we report a study of such resonance modes in KCl:Tl and KCl:Br through specific-heat measurements. As was first theoretically shown by Lehman and DeWames[5] and independently by Kagan and Iosilevskii,[6] a low-frequency resonance mode should substantially enhance the crystal-lattice specific heat at low temperatures. This prediction has later been confirmed experimentally in a few cases for doped metals.[7-9] In metals one has, however, the extra difficulty with the electronic contribution to the specific heat, which one has to subtract to get the true lattice specific heat, a procedure which adds to the uncertainty. The analyses of specific-heat data obtained on ionic crystals are more straightforward since contributions from mechanisms other than the lattice vibrations can usually be neglected.

The systems KCl:Tl and KCl:Br were chosen for several reasons. First, the ratio between impurity mass and host mass (the latter here taken as the mean of m_{K^+} and m_{Cl^-}) is reasonably high, 5.5 and 2.1, respectively. Second, the potassium and chlorine atoms have nearly the same masses and therefore the host lattice can be regarded as monatomic to a good approximation. This makes the comparison between experiment and existing theory especially easy. Third, both systems show a high degree of solubility of the constituents in each other (KCl and KBr actually form a solid solution at all compositions). This fact is quite essential in this experiment, as one needs a fairly high concentration of the impurity (at least 0.5 mole%) in order to obtain a sufficient enhancement of the specific heat.

II. EXPERIMENTAL

The single crystals used in this study were grown in the Crystal Growing Facility of the Cornell Materials Science Center. Crystals of KCl-KBr were seed pulled from the melt using a heated chimney placed over the crucible to maintain the crystal at a high temperature immediately after solidification, thus preventing the crystal from cracking due to thermal shock.[10] To reduce strains in the crystals, they were annealed in argon for several hours 50 °C below their melting point before the measurement.

In order to obtain the desired high concentrations of thallium in KCl (1–5 mole%), it was necessary to grow the KCl:Tl crystals by the Bridgman technique. The reason for this is the high vapor pressure of the thallium chloride at the melting point of KCl. The starting material was analytic reagent grade that had been chlorine treated. The growth took place in a quartz tube under a low-pressure chlorine atmosphere (20 Torr at room temperature). It was anticipated that the crystal might stick to the walls during solidification and then crack during cooling. Therefore the quartz tube was coated with a thin carbon film. This was done by bubbling nitrogen gas through acetone before passing it into the tube, which was held at a temperature of 850 °C. In a later attempt to grow a crystal without carbon coating, it was found that sticking could be prevented if the cooling rate was slow enough and therefore the coating procedure was abandoned.

Although the phase diagram of KCl-TlCl, as determined by Sandonnini,[11] indicates the constituents to be soluble in each other at all concentrations, an attempt to grow a KCl:Tl crystal with 8-mole% thallium in it resulted in a crystal that appeared "milky," probably due to thallium precipitation. The crystal containing 5-mole% thallium still appeared clear. We therefore conclude that the solubility limit for thallium in KCl lies between 5 and 8 mole%.

Impurity concentrations were determined from the content in the melt. For KCl:Br, Baumann and Pohl[12] found the concentrations determined by chemical analysis to be equal to those determined from the melt. In the case of KCl:Tl, we argue that the impurity concentration in the melt is close to the true doping content in the crystal, since the quartz tube was sealed and all the TlCl had been dissolved in the crystal.

The technique for measuring the specific heat is standard. The samples, whose masses varied between 15 and 50 g, were suspended on thin cotton threads and only made contact with the heat sink through the leads to heater and thermometer. The heater leads were niobium wires, 30 cm long and 0.1 mm in diameter. The heater itself was made of nichrome wire with 1000-Ω resistance, and was glued to the sample with a small amount of GE 7031 varnish. The leads connecting the thermometer to the binding post were enameled constantan wires, 50 cm long and with a diameter of 0.05 mm. The time constants so obtained for the heater and thermometer leads were much longer (100 times or more at most temperatures) than the duration of the heat pulse (typically 2–10 sec).

For the initial cooldown, a helium-gas-operated mechanical heat switch[13] was used. In the closed position, a thick copper wire with one end glued to the sample was forced to make contact with the copper post, which allowed the sample to be cooled down reasonably fast. In the open position, the contact between wire and post was broken and the sample was thermally isolated except for the contact through heater and thermometer leads as mentioned above. To prevent the thick copper wire from freezing to the post, it was found necessary to close the heat switch only after nitrogen had been filled into the helium Dewar for precooling.

Carbon resistors (Allen Bradley, 0.1 W) were used to record temperatures and temperature differences. From 1 to 10 °K, a 100-Ω resistor was found to have a convenient R-versus-T characteristic, whereas from 5 °K up, a 1500-Ω resistor was used. In the overlap region (5–10 °K), both resistors were read simultaneously and they were always found to give indistinguishable specific-heat values.

The temperature calibration was carried out in three steps. Below 4.2 °K, the vapor pressure of He^4 was used as a temperature standard. Above 12 °K, the calibration was done against a Leeds and Northrup platinum resistance thermometer with a residual resistance ratio of 5.2×10^{-4}. This thermometer has been used in earlier work in this laboratory.[14] The intermediate region 4.2–12 °K was covered using a three-parameter interpolation formula given by Clement and Quinnell.[15] To check the consistency of this formula, resistance readings for four carbon resistors were taken simultaneously at a number of points between 4.2 and 12 °K. From a least-squares fit to the interpolation formula (using a few points above 12 °K and a few below 4.2 °K), the three parameters were fixed and the formula was then used to obtain temperatures corresponding to the resistance values recorded. The disagreement in interpolated temperatures between the four resistors was never larger than 10 m °K. The estimated uncertainty in all temperature calibrations is 0.4%.

Carbon radio resistors are known to change their R-versus-T characteristic with time and treatment. In an attempt to minimize this as far as possible, the resistors were cycled in a sealed-off metal tube between room temperature and helium temperature more than twenty times prior to calibration. Once their leads had been connected to the binding posts in the cryostat, they were not unsoldered again until all runs were completed. The time drift of the carbon resistors was checked from time to time against a germanium resistor, used as a secondary thermometer permanently mounted in the cryostat, and the drift was found to be less than 0.1% over a period of three months.

Great care was taken in this investigation to assure that the pure and doped crystals were measured under nearly identical conditions. This was done by using the same pair of carbon resistors for both measurements, by taking the specific-heat points at the same temperature, and by taking ΔT the same size (approximately 1% of T). This means that any systematic error inherent in the measuring procedure should affect both measurements in the same way and to the same extent, and thus cancel when ΔC is formed. The resulting precision in the specific-heat points is consequently very high, certainly better than 1%. This is manifested in the low scattering of $\Delta C(T)$ from a smoothed curve.

The over-all accuracy of the measured specific-heat function $C(T)$ depends mainly on the accuracy of T, that is, the accuracy of the temperature calibration of the thermometers, and of ΔT through the measurement of ΔR. As mentioned above, the uncertainty of T is estimated to be 0.4%, which would contribute an error of 1.2% to $C(T)$. The smallest ΔR recorded are of the order of 10 Ω and are measured to 2×10^{-2} Ω, which means an error in ΔT of 0.2%. Other quantities measured, such as voltage drop across the sample heater, current through the heater, and the duration of the heat pulse, were all measured with an accuracy better than 0.1%. We therefore estimate the over-all uncertainty in $C(T)$ to be ± 2%.

III. RESULT AND DISCUSSION

A. KCl:Tl

Figure 1 summarizes the measurements on KCl:Tl. Three doped crystals were measured, containing 1-, 3-, and 5-mole% thallium. Shown is ΔC, as defined by

$$\Delta C(T)=C(T)-C_0(T)\ , \qquad (1)$$

where $C_0(T)$ is the specific heat of the undoped host crystal and $C(T)$ refers to the doped crystal. In order to estimate the magnitude of the specific-heat enhancement from the graph, the measured specific-heat function for pure KCl has been included in the same graph and the Debye T^3 line, determined from a least-squares fit to the very low-temperature portion of $C_0(T)$ (below 4 °K), has been indicated.

ΔC increases steadily with temperature for all three concentrations, up to approximately 10 °K. The maximum enhancement $\Delta C/C$ is roughly 9, 30, and 43% for the 1, 3, and 5% crystals, respectively, and occurs in all cases around 9 °K. Above 10 °K, a leveling off of ΔC takes place and finally a drop is noticeable. In fact, all three curves show a crossover for ΔC to slightly negative values, a tendency that persists up to the highest temperatures measured (approximately 50 °K). This crossover occurs for the 1% curve at 13 °K, for the 3% curve at 23 °K, and for the 5% curve at 24 °K.[16]

Kagan and Isoilevskii[6] give, for the enhancement

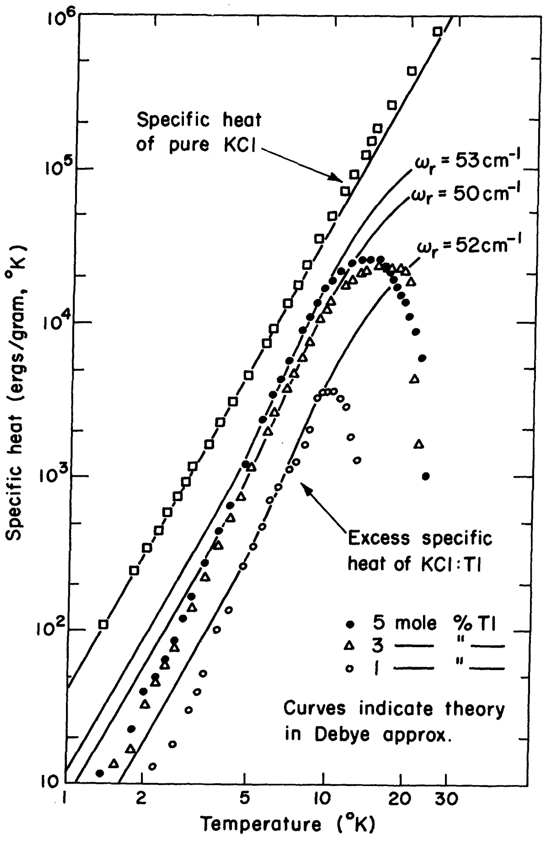

FIG. 1. Specific-heat enhancement in KCl : Tl (1-, 3-, and 5-mole% Tl⁺). Also shown is the specific heat of pure KCl.

of the lattice specific heat due to a heavy isotopic impurity of concentration $\eta\,(\eta \ll 1)$,

$$\Delta C(T) = -3\eta \int_0^1 \frac{\partial z(x)}{\partial x}\, \varphi(x, T)\, dx \ , \tag{2}$$

where

$$\varphi(x, T) = kx\left(\frac{\hbar\omega_{\max}}{kT}\right)^2 \exp\left(\frac{\hbar\omega_{\max}\sqrt{x}}{kT}\right) \times\left[\exp\left(\frac{\hbar\omega_{\max}\sqrt{x}}{kT}\right) - 1\right]^{-2} , \tag{3}$$

$$z(x) = -\frac{1}{\pi}\cot^{-1}\left[\frac{1}{\pi|\epsilon|xg(x)}\left(1 + |\epsilon|\,x\int_0^1 \frac{g(x')\,dx'}{x - x'}\right)\right] , \qquad -1 < z < 0 \tag{4}$$

where $\omega_{\max}$ is the upper limit of the phonon spectrum of the matrix, $x = \omega^2/\omega^2_{\max}$; $g(x)$ is the distribution of the squares of the matrix frequencies, normalized to unity; $\epsilon = 1 - m'/m$, where m' is the mass of the impurity atom and m the mass of the host atom; and k is Boltzmann's constant.

Formula (2) is based on the assumption of a monatomic host lattice. By assuming a Debye frequency spectrum for the host lattice, one can reduce expression (2) to [17]

$$\Delta C = 3\eta k\left(\frac{\Theta}{T}\right)^2 \int_0^1 \frac{x^{3/2}(3x_r - x)}{4(x_r - x)^2 + \pi^2 x^3}\, \frac{e^{(\Theta/T)\sqrt{x}}}{(e^{(\Theta/T)\sqrt{x}} - 1)^2}\, dx, \tag{5}$$

where $\Theta = (\hbar/k)\omega_D$ is the Debye temperature and $x_r = \omega_r^2/\omega_D^2$, ω_r is the frequency associated with the resonance mode under study, given by the expression

$$\omega_r = \omega_D/(3|\epsilon|)^{1/2} \ . \tag{6}$$

The integral in (5) was evaluated using ten-point Gaussian quadrature. ω_r was treated as an adjustable parameter and was determined from the best fit of (5) with the experiment. Figure 2 gives an idea of the degree of agreement between theory and experiment. From this figure and from the uncertainty in the Tl$^+$ concentrations, the error in ω_r is estimated to be 15%.

The isotopic model fits the general behavior of the measured ΔC up to approximately 10 °K. The mean of the resonance frequencies obtained from the three curves in Fig. 1 is 51 ± 8 cm^{-1}. This value is some 12% higher than the value of 45 cm^{-1} that one calculates from the simple formula (6). The conclusion to be drawn from this comparison is that in this temperature region (1–10 °K) the isotopic impurity model seems to be quite adequate for describing the effect that the resonance mode exerts on the lattice specific heat. This isotopic behavior of the thallium ion in KCl becomes perhaps less unexpected as one recognizes that the values of the ionic radii for potassium and thallium ions are very close: 1.33 Å for K$^+$ and 1.40 Å for Tl$^+$.[18] What is less readily expected is the concentration independence of ω_r (Fig. 1). 5-mole% thallium in KCl means that one has really left the true impurity concentration region and is well on one's way towards an alloy system, in which ΔC by no means can be expected to be independent of concentration. The validity of the isotopic model for an alloy system will be discussed further in Sec. III.

Our results support the conclusions drawn by Baumann and Pohl[12] in their interpretation of their thermal conductivity data. From the best fit of theory with experiment, they determined a resonance frequency of 45 cm^{-1}, the same value as formula (6) predicts. The results in the present paper provide independent evidence that their way of interpreting the thermal conductivity data was indeed correct.

The resonance mode in KCl:Tl is known to be of

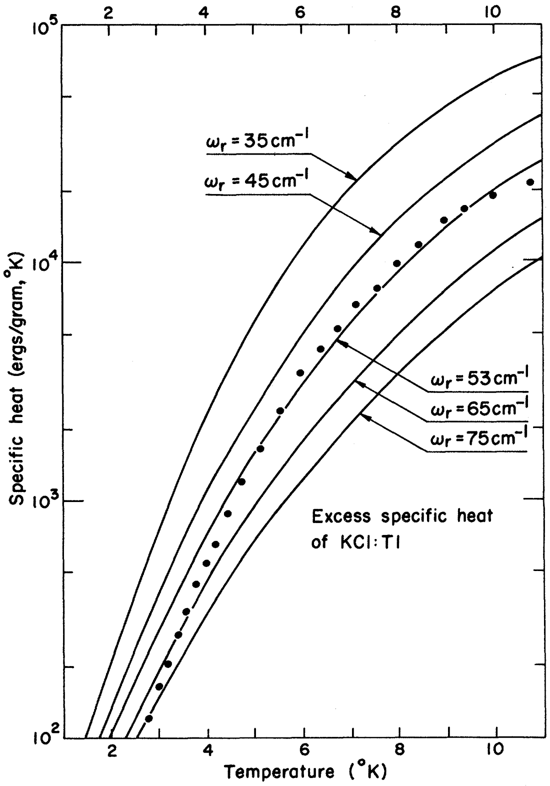

FIG. 2. Comparison between experimental and calculated specific-heat enhancements for KCl : Tl (5-mole% Tl$^+$).

symmetry T_{1u} (in the isotopic approximation) and consequently ought to be optical active.[12] The failure to detect any strong absorption line for this system in the far infrared was discussed by Baumann and Pohl.[19] They reached the conclusion that the T_{1u} mode is very strongly damped and hence the absorption band is too broad to be detectable in the infrared. A recent calculation for KCl:Tl by Page,[20] making use of the Green's-function technique in the mass defect model and using a realistic frequency spectrum for the host lattice, indicates, however, that the half-width of the expected absorption line (with a resonance frequency calculated to be about 43 cm^{-1}) is small enough (approximately 10 cm^{-1}) so that even a weak absorption line should be detectable with improved techniques. Renewed infrared absorption measurements[21] have revealed, in fact, a weak line in KCl:Tl at about 39 cm^{-1} and with the same half-width as calculated by Page.

Very recently additional evidence for the isotopic behavior of the thallium ion in KCl was given by Harley, Page, and Walker.[22] They studied the Raman scattering spectra for Tl^+ in KCl, KBr, and KI and found that the Raman-active even modes also agreed with the isotopic model.

At temperatures above 10 °K, expression (5) is no longer able to describe the behavior of the experimental data (Fig. 1). The reason for this is probably the nonvalidity in this temperature region of the Debye spectrum approximation for the host lattice. That the measured ΔC becomes negative means that the phonon density of states in the frequency range corresponding to these temperatures now has a value lower than in the pure crystal. The excess density of states constituting the resonance mode in other words causes a "hole burning" in the density of states of the host crystal at frequencies in the neighborhood of the resonance of the mode itself. Such an effect was demonstrated by Mozer and Maradudin[23] in their calculation of the frequency spectrum for an isotopically disordered crystal. By the use of a more realistic frequency spectrum $g(x)$ in relation (2), one may be able to account for the negative ΔC, but this has not yet been attempted.

B. KCl:Br

Figure 3 shows the result for KCl:Br (5-mole% Br^-). A comparison with KCl:Tl shows that the enhancement $\Delta C/C$ here is considerably less. This is in accordance with the smaller ratio between impurity and host masses (~2.1). The general behavior of ΔC is otherwise similar, although for KCl:Br ΔC never becomes negative and only at the highest temperatures measured (30 °K) is there a slight indication of a leveling off.

The resonance frequency, determined in the same way as before, is for this system 110 ± 10 cm^{-1}, whereas Eq. (6) gives 87 cm^{-1}. Page,[20] however, within his model as mentioned earlier, has shown that the resonance condition for this system is satisfied at 113 cm^{-1}. The difference between the two calculated values is obviously due to the relative sensitivity of the calculation to the details of the phonon spectrum at higher frequencies. Weber and Siebert[24] measured the infrared absorption of KCl:Br and detected a strong peak at 108 cm^{-1}. They concluded, however, that this peak is not caused by a resonance mode but rather by a maximum in the density of states of the host at this frequency. Our present result cannot be explained in the same way, as $\Delta C(T)$ reflects only changes in the density-of-states function of the pure crystal, caused by the introduction of impurity atoms. We therefore argue that the recorded specific-heat enchancement is caused by a true lattice resonance mode.

C. KCl_{1-x}-KBr_x

In Sec. III A, it was shown that the resonance frequencies determined within the isotopic model are independent of the Tl^+ concentrations up to 5 mole%.

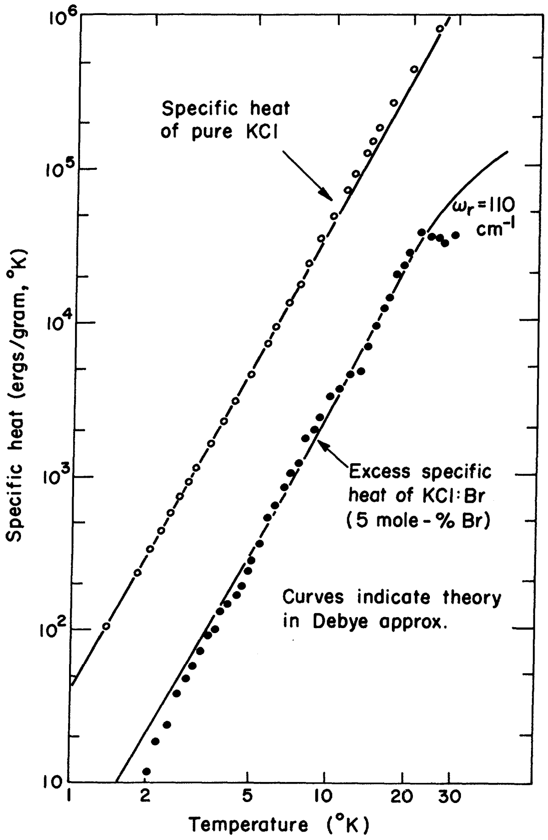

FIG. 3. Specific-heat enhancement in KCl : Br (5-mole% Br^-). Also shown is the specific heat of pure KCl.

To get some idea about the validity of the model for even higher impurity concentrations and ultimately for an alloy system, the specific heat for the solid solution KCl_{1-x}-KBr_x was measured at four intermediate compositions, $x = 0.05$, 0.20, 0.50, and 0.80. The results of these measurements are shown in Fig. 4, where the effective Debye temperatures are plotted versus temperature, both on a linear scale. The well-known minimum in Θ_D that most alkali halides exhibit and that was first accounted for by Blackman[25] occurs for KCl at around 18 °K and for KBr at 13 °K. For the intermediate compositions, the minimum is gradually shifted and no true structure is noticeable.

The specific heats of pure KCl and KBr were also measured (Fig. 4). A comparison with the accepted literature values as given by Berg and Morrison[26] shows an excellent agreement for KBr (within the scatter of the points), while our KCl data are somewhat higher in the temperature range 10–20 °K. Below 10 °K and above 20 °K the disagreement is only slight, and above 35 °K there is no disagreement at all. A similar trend for pure KCl has recently been reported by Kirkham and Yates,[27] who found values at 25 °K somewhat higher than those of Berg and Morrison.

From the experimental curves in Fig. 4, an extrapolation of Θ_D to $T = 0$ was made and $\Theta_D(0)$ was then plotted versus composition x (the points in Fig. 5).

As can be seen, there is no linear dependence of $\Theta_D\,(T = 0)$ with composition. Iosilevskii[28] has given

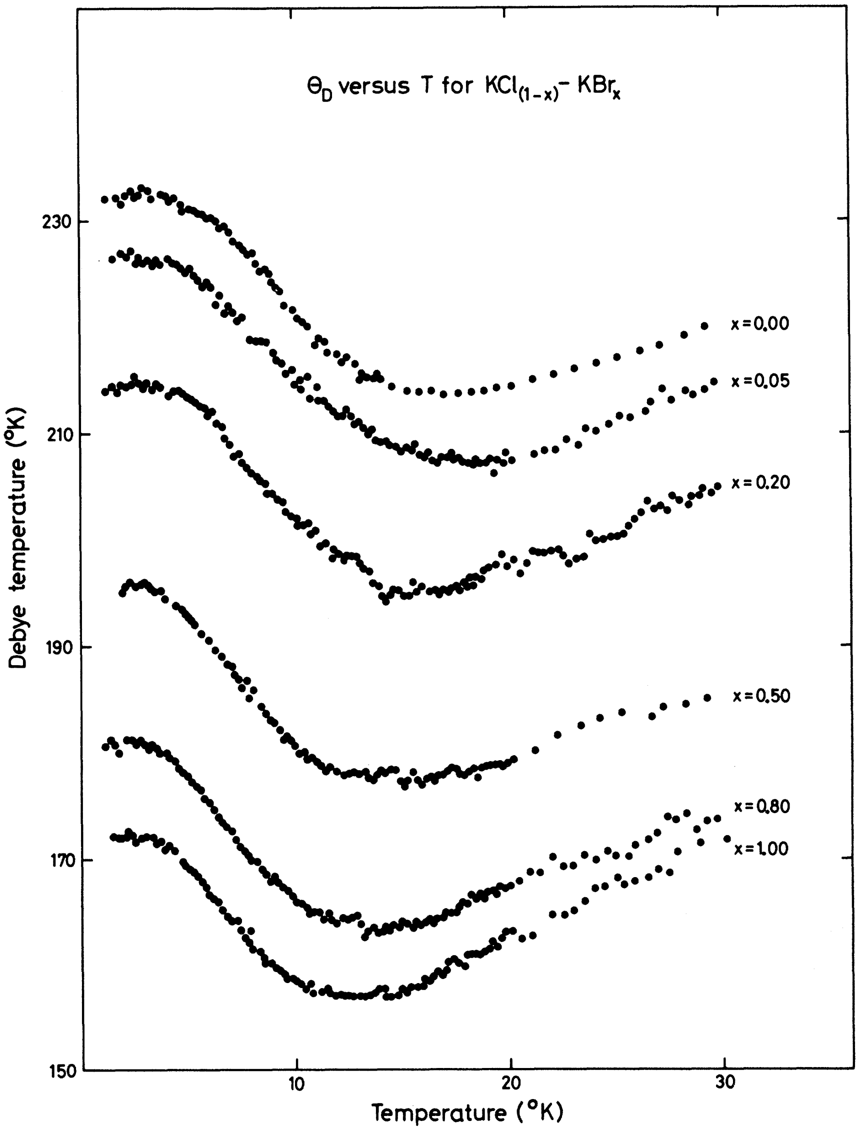

FIG. 4. Effective Debye temperature as a function of temperature for the solid solution KCl_{1-x}-KBr_x for different compositions x.

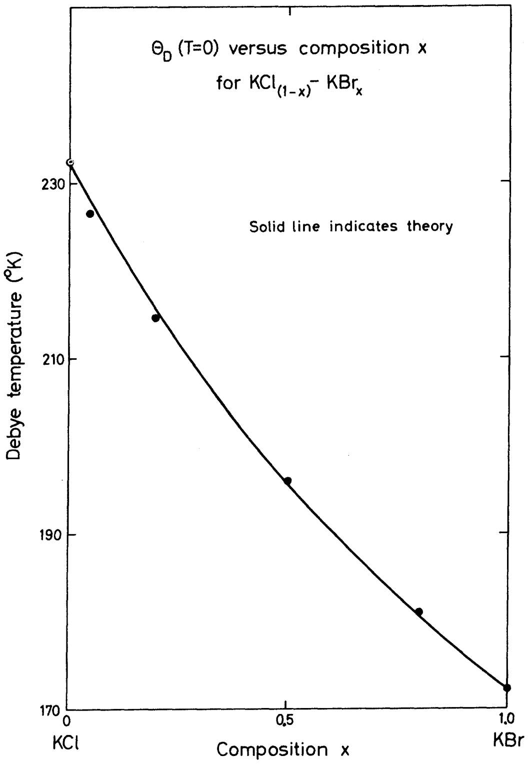

FIG. 5. Debye temperatures at T = 0 as a function of composition x for KCl_{1-x}-KBr_x, obtained by extrapolation from Fig. 4. The solid line is calculated from formula (9).

an interpolation formula for the Debye frequency ω_D at low temperatures for a solid solution as a function of composition x,

$$1/\omega_D^2 = \sum_{a=1}^{t} x_a/\omega_{aD}^2 , \qquad (7)$$

where ω_{aD} is the Debye frequency of the pure component a and t is the number of components in the solid solution. By use of the definition relation for the Debye temperature

$$\Theta_D = (\hbar/k)\omega_D , \qquad (8)$$

and with $t = 2$ as in our case, one gets (x is now the relative concentration of KBr in the solid solution)

$$1/\Theta_D^2 = x/\Theta_{D\,\mathrm{KBr}}^2 + (1-x)/\Theta_{D\,\mathrm{KCl}}^2 . \qquad (9)$$

With $\Theta_{D\,\mathrm{KBr}}(0) = 172$ °K and $\Theta_{D\,\mathrm{KCl}}(0) = 232$ °K as independent parameters, $\Theta_D = \Theta_D(x)$ was calculated from (9) (solid line in Fig. 5). As can be seen, the agreement between theory and experiment is good. This indicates that the isotopic approximation, which Eq. (9) was based on, is well justified for a solid solution at all compositions at least in the limit of very low temperatures.

IV. SUMMARY

In this paper, our aim has been to demonstrate the possibility of using precise specific-heat measurements to study impurity modes in ionic crystals. The resonance frequencies determined by this method are in general agreement with those obtained by means of other techniques. Although the resolution in specific-heat spectroscopy is less than the resolution obtainable in ir work, the method presented here can serve as a complement to the infrared technique. The advantage is that the specific heat "sees" all kinds of modes, whereas the infrared absorption registers only the infrared-active ones. In addition, this investigation also demonstrates that it is possible to get information about the effect that a low-lying mode (as the one in KCl:Tl) exerts on the "background" phonon density-of-states function. For a full understanding of this effect, more theoretical work is obviously needed.

ACKNOWLEDGMENTS

To Professor Robert O. Pohl I would like to express my deep gratitude for suggesting this study, for his guidance throughout the course of the work, and for the generous hospitality extended to me during my stay at Cornell. The cheerful support from D. J. Channin, A. T. Fiory, W. M. Goubau, T. McNelly, and R. J. Rollefson is gratefully acknowledged. I am indebted to Professor J. B. Page, A. M. Kahan, and Professor A. J. Sievers for permission to quote their results prior to publication. I am also grateful to the Cornell Materials Science Center for the excellent technical facilities put at my disposal. I would like to thank the Committee for Solid State Physics, Swedish Atomic Research Council, for a scholarship that made this work possible.

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†Research mainly supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)2391, Technical Report No. NYO-2391-113.

*Additional support was received from the Advanced Research Projects Agency through the use of the space and technical facilities of the Materials Science Center at Cornell University.

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