

coordination cube. The oxygen cubes occur in the unit cell in six inequivalent positions, with one local $\langle 100 \rangle$ direction of each along one of six different $\langle 110 \rangle$ directions of the unit cell. Figure 1 is drawn with the unit cell $\langle 100 \rangle$ directions used as coordinates and shows only one of the six possible local configurations.

Second, the magnetic axis in Figs. 2 through 11 is determined by the direction of M_{Fe} , not of the applied magnetic field. Since the absolute energy of the lowest-lying level is a strong function of the direction of magnetic axis (differing by 8 cm^{-1} from $[100]$ to $[111]$ in Dy^{++}), there is a marked tendency for the rare earth ion to twist the polarization of the Fe ions to which it couples away from H_{external} . The macroscopic

magnetic properties will have the symmetry of the unit cell, but strong distortions of M within the unit cell must be expected.

Finally, the idealizations of the local symmetry mentioned earlier are again reiterated to indicate the degree of uncertainty which must reside in any calculation of properties of the total actual system.

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Properties of Alkali Halide Crystals at Low Temperatures*

T. H. K. BARRON, *Department of Physical and Inorganic Chemistry, The University, Bristol, England*

AND

J. A. MORRISON, *Division of Pure Chemistry, National Research Council, Ottawa, Canada*

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Recent experimental results on low-temperature heat capacities and elastic constants of alkali halide crystals are examined for evidence of anharmonic contributions. It is concluded that if such effects are present their contribution to the characteristic temperature at 0°K is less than that of uncertainties in the experimental results.

SOME new experimental results on low-temperature properties of alkali halide crystals were recently obtained at the Rice Institute, and reported in this journal. Norwood and Briscoe¹ have measured elastic properties of KCl and KI over the temperature range 4° to 300°K , and Scales² has measured heat capacities of LiF and KI over the range 2° to 7°K . One aim of this work was to compare the limiting characteristic temperatures, Θ_0 and $\Theta(\text{elastic})$, given, respectively, by calorimetric and elastic measurements as T approaches 0°K . These should be equal provided that the lattice vibrations are purely harmonic; but recent work by Ludwig³ has suggested that a combination of zero-point energy and anharmonicity may cause differences of the order of 1%. The conclusion reached in the Rice Institute papers is that some of the experimental results may support Ludwig's theory.

It is clear that modern refinements in experimental technique are beginning to make it worth while to look for anharmonic effects in the heat capacity of crystals,⁴ but in order to detect these it is important that the consequences of *harmonic* lattice theory be kept clearly

in mind during the examination and interpretation of experimental results. We believe that the Rice Institute papers are open to criticism in this respect and that some of their arguments could be seriously misleading; this applies particularly to Scales's estimation of Θ_0 from his experimental results.

THE ESTIMATION OF Θ_0

Scales starts by assuming that below a temperature of the order of $\Theta_0/50$ a "true T^3 region" is reached, in which $C_v = aT^3$; in this region Θ_D would be effectively constant and equal to Θ_0 . Now this assumption neglects the effect of dispersion on the lattice waves of low frequency, which in fact introduces further terms in higher powers of T into the expansion for the heat capacity. The contribution of such terms does not in general suddenly disappear at some finite temperature, as is suggested by Scales's graph of Θ_D for KI (his Fig. 6). On the contrary, Θ_D must approach a constant value asymptotically according to the expansion

$$\Theta_D = \Theta_0 \{ 1 - A(T/\Theta_0)^2 + B(T/\Theta_0)^4 \dots \}; \quad (1)$$

this is equivalent to the quite general expansion for the lattice heat capacity

$$C_v = aT^3 + bT^5 + cT^7 + \dots \quad (2)$$

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¹ M. H. Norwood and C. V. Briscoe, *Phys. Rev.* **112**, 45 (1958).

² W. W. Scales, *Phys. Rev.* **112**, 49 (1958).

³ W. Ludwig, *J. Phys. Chem. Solids* **4**, 283 (1958).

⁴ Flubacher, Leadbetter, and Morrison, *Phil. Mag.* **4**, 273 (1959).

Whether or not the change in Θ_D with temperature is observable over a certain range depends upon the value of A and of the other coefficients in the expansion, and of course upon experimental uncertainty. Scales's assumption of a region of constant Θ_D below $\Theta_0/50$ is based on a very common but most unfortunate misunderstanding of Blackman's work. Blackman^{5,6} investigated the shape of the lattice frequency spectrum at low frequencies for a number of different crystalline models, and concluded that no general prediction could be made of the sign and magnitude of A . As a rough guide, however, one can say, not that Θ_D will be constant below $\Theta_0/50$, but that its total variation is unlikely to be much more than 1%.⁵ Thus if Θ_0 is required to within 1% or better, it is necessary to consider the variation of Θ_D below $\Theta_0/50$. In another paper⁷ we have examined this whole matter in considerable detail.

While great care is thus needed in interpreting the results for KI, the temperature range of Scales's measurements on LiF falls well below $T = \Theta_0/50$, so that sufficiently accurate measurements would be expected to fix Θ_0 to within a few tenths of 1%. In general, however, low-temperature calorimetry becomes increasingly difficult and less accurate in the region $T < \Theta_0/100$. Where possible, therefore, results over a wider range of temperatures should be used to help determine Θ_0 . It is clear from Eq. (1) that a sensitive method of plotting results at low temperatures is to plot Θ_D against T^2 : this should give a *smooth curve* whose intercept with the axis $T^2 = 0$ will give Θ_0 , while the slope can be used to derive A . We have shown⁷ how an equivalent method (C_v/T^3 is plotted against T^2) makes use of results in the region $T < \Theta_0/25$. By comparison, a plot of C_v against T^3 is very insensitive.

This method of *smooth* extrapolation (of the graph of C_v/T^3 against T^2) has been used⁸ to obtain Θ_0 for several alkali halide crystals. The value derived for KI was $132.3 \pm 1.0^\circ\text{K}$, which is to be compared with Scales's result of 128.3°K . Reference to Fig. 6 of Scales's paper shows that the major part of the difference is to be ascribed to his assumption of a strict T^3 law for $T < 3.5^\circ\text{K}$, which puts great weight on the measurements at the lowest temperatures at the expense of those in the range $4^\circ < T < 7^\circ\text{K}$. It is important also to notice that his value of Θ_0 implies an unexpectedly sharp curvature in the graph of Θ_D against T at about 3.5°K .

To some extent a similar criticism can be made of the discussion of the results for LiF. Taken by themselves Scales's results indeed indicate his estimate of Θ_0 ($\sim 722^\circ\text{K}$), and moreover they are in good agreement with the lowest temperature results of Clusius and

Eichenauer⁹; but again it is important to realize that acceptance of these results involves an unexpectedly sharp curvature in the Θ_D versus T graph at about 20°K . We have discussed this example in detail elsewhere,⁷ and have shown that a combination of Clusius and Eichenauer's results at higher temperatures and Martin's¹⁰ for $T < 20^\circ\text{K}$ gives a smooth curve for C_v/T^3 against T^2 and suggests that Θ_0 is about 743°K , three percent higher than the value estimated by Scales ($722 \pm 6^\circ\text{K}$).

There is therefore conflicting evidence for the behavior of C_v for LiF below 20°K . The results of Scales and of Clusius and Eichenauer indicate that there is a true T^3 region up to about $T = \Theta_D/35$, after which Θ_D suddenly starts to decrease; while Martin's results suggest a smooth variation of Θ_D . The sharp curvature could be explained either if A (and B) in Eq. (1) were small or by a phase transition. On the other hand, the smooth variation seems to us more likely, especially when the results are compared with those for other alkali halides and with theoretical work on ionic lattices.

THE ESTIMATION OF Θ (ELASTIC)

The calculation of Θ (elastic) from elastic constants involves the averaging of the inverse cube of the sound velocity over different directions in the crystal. Norwood and Briscoe¹ do this in two ways: by using de Launay's tables¹¹ for cubic crystals, and by using the semi-analytical "Alberta" method of Betts, Bhatia and Wyman¹²; the answers differ by about $1\frac{1}{2}\%$, and are quoted as having equal authority. In fact, a clear distinction can be drawn between the two methods. De Launay's tables are obtained by straightforward numerical integration over a large number of different directions in the crystal. Where they have been compared with other accurate calculations, the tabulated values have been found reliable to within at least 0.01%. Provided that care is taken over the interpolation (by drawing curves or by using a suitable formula), they should provide accurate results with errors of at most a few tenths of 1%. By contrast, the "Alberta" method usually takes fewer directions in the crystal, but makes more use of the crystal symmetry. It is more general than de Launay's tables, since if the dispersion relations in a few crystal directions are known it can be used to estimate not only Θ_0 but also A of Eq. (1). (See, for example, Horton and Schiff.¹³) In the form quoted by Norwood and Briscoe¹ it is, however, only accurate to within at best about 1%,¹⁴

⁹ K. Clusius and W. Eichenauer, *Z. Naturforsch.* **11a**, 715 (1956).

¹⁰ D. L. Martin, *Phil. Mag.* **46**, 751 (1955).

¹¹ J. de Launay, *J. Chem. Phys.* **24**, 1071 (1956); **30**, 91 (1959).

¹² Betts, Bhatia, and Wyman, *Phys. Rev.* **104**, 37 (1956).

¹³ G. K. Horton and H. Schiff, *Can. J. Phys.* **36**, 1127 (1958).

¹⁴ Better accuracy is achieved in a later paper by E. E. Budzinski and H. Schiff [*Can. J. Phys.* **35**, 507 (1957)].

⁵ M. Blackman, *Proc. Roy. Soc. (London)* **A149**, 117 (1935).

⁶ M. Blackman, *Proc. Cambridge Phil. Soc.* **33**, 94 (1937).

⁷ T. H. K. Barron and J. A. Morrison, *Can. J. Phys.* **35**, 799 (1957).

⁸ Barron, Berg, and Morrison, *Proc. Roy. Soc. (London)* **A242**, 478 (1957).

and so in preference de Launay's tables should always be used to obtain Θ (elastic) for cubic crystals.

CONCLUSION

Revised values of Θ_0 and Θ (elastic) for the three salts mentioned in the Rice Institute papers are given in Table I. [Θ (elastic) for LiF has been obtained from the elastic constants of Briscoe and Squire¹⁵ using de Launay's tables. The value of 743° quoted in reference 7 was derived from their preliminary results.¹⁶] It will be seen that if Θ_0 is derived by extrapolating smoothly a graph of C_v/T^3 against T^2 , then for each salt Θ_0 and Θ (elastic) agree well within the limits of experimental accuracy; there is no indication that Θ (elastic) > Θ_0 (as suggested by Ludwig's calculations), although the limits of accuracy would in fact permit a difference of up to 1%. On the other hand, if Scales's values of Θ_0 for KI and LiF are chosen, we find that Θ (elastic) > Θ_0 by about 2%.

The example of LiF is of particular interest because the lower estimate of Θ_0 (722°K) is quoted by Ludwig

¹⁵ C. V. Briscoe and C. F. Squire, *Phys. Rev.* **106**, 1175 (1957).

¹⁶ C. V. Briscoe and C. F. Squire, *Bull. Am. Phys. Soc. Ser. II*, **2**, 18 (1957).

TABLE I. Characteristic temperatures at 0°K for KCl, KI, and LiF.

	KCl	KI	LiF
Θ (elastic)	236 ±1	131 ±2	735±5
Θ_0 (extrapolated)	235.1±0.5 ^b	132.3±1 ^b	743±7 ^c
Θ_0 (Scales ^a)	...	128.3	722±6

^a See reference 2.

^b See reference 8.

^c See reference 7.

(p. 300 of reference 3) as providing some confirmation for his theory; but as we have seen, measurements in the important range of temperatures below 20°K disagree. The resolution of this uncertainty by experiments of more reliable accuracy would be very desirable, since it would firmly settle both the shape of the C_v/T^3 curve (relevant to the harmonic theory) and the difference between Θ_0 and Θ (elastic)¹⁷ (relevant to the anharmonic theory).

¹⁷ It should be noted that Ludwig³ finds that the classical relation between elastic constants and sound velocities is no longer strictly valid for longitudinal waves. If so, the values of c_{11} and c_{12} given by the pulse technique may not be exactly equal to the static values; however, no numerical estimate is given of the magnitude of this effect. Fortunately, Θ (elastic) depends mainly upon c_{44} , which is determined solely from the velocity of transverse waves.

Diffusion Measurements in the System Cu-Au by Elastic Scattering

ROBERT F. SIPPEL

Field Research Laboratory, Socony Mobil Oil Company, Dallas, Texas

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A broad-range magnetic spectrograph has been used to study the diffusion of gold into copper in the temperature range 360–500°C by elastic scattering of protons and deuterons. This is a new technique in solid diffusion measurements and should have fairly wide applicability in intermetallic diffusion. This investigation extends the data a factor of 10^6 below the sectioning range. These results together with data of sectioning observers, show the Arrhenius law to be approximately valid over a range in D of 5×10^8 . A precise fit to all the data requires a slight upward curvature. In the temperature range studied here, we obtain $Q = 45,750 \pm 750$ cal/mole and $D_0 = 0.104 \pm 0.06$ cm²/sec. This represents a decrease of about 4000 cal/mole from the most precise data in the sectioning range. This curvature is attributed to diffusion along internal surfaces, although the possibility of multiple diffusion mechanisms still remains.

INTRODUCTION

ALTHOUGH considerable effort has been brought to bear on the problem of solid diffusion measurement and many ingenious methods have been used, the sectioning technique has become more or less standard because of its precision and wide applicability in metallic systems. However, because the depth of investigation (≈ 0.01 cm) is so large, the method is effectively limited to the range of $D > 10^{-12}$ cm²/sec. This, coupled with the upper limit imposed by melting point, has effectively limited the range of data to a few orders of magnitude in many cases. Nowick¹ and many others have pointed

out the seriousness, for theoretical purposes, of the lack of sufficiently accurate data over sufficiently wide range. Methods extending the range significantly below 10^{-12} cm²/sec have been either indirect or else limited to specific systems having unique properties.^{2–5} Extension of the data to low temperatures is of importance not only for increased accuracy, but also to explore for possible deviations from the Arrhenius law, indicating multiple mechanisms of diffusion, such as the suggestion of Lazarus of the possibility of barrier penetration in

² G. von Hevesy and W. Seith, *Z. Physik* **56**, 790 (1929).

³ E. Cremer, *Z. Physik Chem.* **B39**, 445 (1938).

⁴ W. Jost, *Z. Physik Chem.* **B9**, 73 (1930).

⁵ C. A. Wert, *Phys. Rev.* **79**, 601 (1950).

¹ A. S. Nowick, *J. Appl. Phys.* **22**, 1182 (1951).