$\lesssim 300°$K, the approximation of a constant Debye temperature would appear to be a poor one. However, according to specific-heat measurements (L. J. Vieland and A. Wicklund, to be published), the Debye temperature actually varies quite slowly in this temperature range.

[7]See, for example, J. M. Ziman, Electrons and Phonons (Oxford University Press, London, England, 1962), p. 264-270.

[8]It should be pointed out that this "impurity" term is indistinguishable from one that would arise from the interaction of electrons with an optical mode whose frequency is vanishingly small. That such a mode may exist in these metals has been suggested by W. Rehwald (to be published).

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[13]Actually, the first term on the right-hand side of Eq. (7) should be multiplied by $[1-N_0 V_C (1-\frac{1}{2}\alpha) F_\alpha (T)]^{-1}$ to take into account the enhancement of χ due to the Coulomb repulsion V_C. However, because of the scatter of experimental data, we are unable to make a definite choice of V_C (except to say that $\frac{1}{2} N_0 V_C \lesssim 0.5$). We have, therefore, set $V_C = 0$; this may lead to an overestimate of N_0 by as much as 20%.

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ENTROPIES AND ENTHALPIES FOR SELF-DIFFUSION IN POTASSIUM BROMIDE

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The measured electrical conductivity of pure KBr is analyzed into anion and cation components in two ways, and the results compared with those obtained by direct diffusion measurements. It is found that analysis of the conductivity using only the intrinsic region is unreliable and leads to an overestimate of the anion and an underestimate of the cation activation entropy and enthalpy.

In a recent Letter in this journal, Fuller and Reilly[1] reported the results of a least-squares analysis of the intrinsic electrical conductivity of RbCl. This analysis gave the enthalpies for both the anion and cation components and the difference between their entropies. The results obtained were striking in that the enthalpy of motion of the cation was markedly smaller than the result obtained by direct measurement, 1.58 eV as opposed to 1.99 eV,[2] and for the extremely large difference of $12k$ between the entropies. The difference in the cation enthalpies was ascribed to a vacancy-pair contribution to the cation diffusion.

We have for some time been engaged in studying the ionic transport properties of both pure and divalent-cation–doped KBr. These studies include measurement of the bromine diffusion using isotope exchange,[3] and potassium diffusion using mechanical sectioning and ac electrical conductivity.

From these measurements the anion-cation vacancy-pair contribution to the observed anion and cation self-diffusion can be calculated. In addition the activation entropies and enthalpies can be resolved into consistent values of the formation and motion entropies and enthalpies. In Table I are listed the activation entropies and enthalpies for the anion, $s_T{}^a$ and $h_T{}^a$, and the cation, $s_T{}^c$ and $h_T{}^c$, calculated in the following ways:

(1) By direct measurement of the bromine and potassium diffusion coefficients. For the anion the vacancy-pair contribution has been subtracted; for the cation the vacancy-pair

Table I. Entropies and enthalpies for self-diffusion in KBr.

Method	$s_T{}^a/k$	$h_T{}^a$ (eV)	$s_T{}^c/k$	$h_T{}^c$ (eV)	$(\Delta s^a - \Delta s^c)/k$
1	9.6	2.22	7.7	1.94	1.9
2	9.9	2.21	6.8	1.91	3.1
3	13.7	2.48	5.8	1.84	7.9

contribution was small enough to be neglected.

(2) By a least-squares analysis of the electrical conductivity, σ, in a "pure" crystal (~1 ppm divalent cation impurity) over the temperature range $570 < T < 970°$K using the equation

$$\sigma T = \frac{4Na^2\nu e^2}{k}\left\{\tfrac{1}{2}c \exp\left(\frac{\Delta s^C}{k} - \frac{\Delta h^C}{kT}\right)\left[\left(1 + \frac{4\exp(s/k-h/kT)}{c^2}\right)^{\frac{1}{2}} + 1\right]\right.$$
$$\left. + \tfrac{1}{2}c \exp\left(\frac{\Delta s^a}{k} - \frac{\Delta h^a}{kT}\right)\left[\left(1 + \frac{4\exp(s/k-h/kT)}{c^2}\right)^{\frac{1}{2}} - 1\right]\right\}, \qquad (1)$$

where the following seven parameters are variables: the divalent impurity content C, the movement enthalpies Δh^a and Δh^C and the movement entropies Δs^a and Δs^C for the anion and cation, and the enthalpy h and entropy s of formation of a Schottky defect. N, e, k, a, and ν have their usual meanings.[4] A value of 3.2 $\times 10^{12}$ cps was used for ν.[5] In crystals containing about 1 ppm of divalent cation impurity we find that impurity-vacancy association can be neglected. In Table I, $s_T{}^a$ is put equal to $\Delta s^a + \tfrac{1}{2}s$ and $h_T{}^a$ equal to $\Delta h^a + \tfrac{1}{2}h$, etc.

(3) By a least-squares analysis of the electrical conductivity in the intrinsic temperature region using the equation

$$\sigma T = \frac{4Na^2\nu e^2}{k}$$
$$\times\left[\exp\left(\frac{s_T{}^c}{k} - \frac{h_T{}^c}{kT}\right) + \exp\left(\frac{s_T{}^a}{k} - \frac{h_T{}^a}{kT}\right)\right]. \qquad (2)$$

The intrinsic region of the conductivity was chosen as being above a temperature of 560°C. This is essentailly the same relative temperature as Fuller and Reilly used in RbCl and is higher than the conductivity "knee" temperature in our specimen, which was about 480°C.

In these calculations no allowance was made for Debye-Hückel interactions. Both Eqs. (1) and (2) were found to fit the data to the same accuracy.

Comparison of the results shows that use of Eq. (2) results in an overestimate of the anion and an underestimate of the cation enthalpy. In addition, the difference between the anion and cation entropies is grossly overestimated. These were also the striking features of Fuller and Reilly's analysis on RbCl and would, in the light of the present results, appear to be a consequence of the type of analysis used. The difficulty in using Eq. (2) in this way seems twofold: firstly, in deciding where, in a continuously curved conductivity plot, the intrinsic conductivity starts; secondly, the inherent difficulty in fitting the sum of two exponentials, with unique parameters, over a limited range of conductivity and temperature. When only electrical conductivity data on pure crystals are available, it seems that a seven-parameter fit using Eq. (1) over a wide temperature range is better. Direct measurement of the diffusion is probably best.

A fuller account of the experimental procedures and results will appear elsewhere.

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