PHYSICAL REVIEW B VOLUME 26, NUMBER 10 15 NOVEMBER 1982

Enhanced thermal conduction associated with formation of the superionic state

R. K. Williams

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 11 August 1982)

High anion mobilities associated with formation of the superionic state in fluorite crystals may lead to a measurable enhancement of the thermal conductivity. The enhancement was estimated for $SrCl_2$, and found to reach a maximum value of about 0.02 W/mK. The temperature dependence of the effect differs from that of ambipolar thermodiffusion of electron-hole pairs. The enhancement due to ionic transport is dependent on the thermodynamics of the anion disordering process, and some experimental tests of the mechanism are suggested.

In nonmetallic crystals, energy is transported by phonons, and, if optical conditions are favorable, photons. In polycrystalline samples phonons usually dominate, and Slack[1] has recently reviewed the literature and theory pertaining to this transport at high temperatures. The purpose of this Communication is to suggest that ionic motion may make an additional contribution to the energy current in nonmetallic materials undergoing a transition to the superionic state. This conduction mechanism, which apparently has not been considered before, is similar to ambipolar diffusion of electron-hole pairs in an intrinsic semiconductor.[2] The experimental basis for the calculation is that Moore *et al.*[3] have recently shown that the thermal conductivity of $SrCl_2$ exhibits a local enhancement in the temperature range associated with the formation of the superionic state.

Dworkin and Bredig[4] observed an anomalous enthalpy increase associated with the Faraday transition in $SrCl_2$ about 20 years ago, and the effect has been the subject of many recent investigations because the disordering leads to fast-ion conduction.[5] The transition is associated with the entropy-driven movement of anions into or toward[6] the cube center position from their normal tetahedral sites, and the rapid change in disorder with temperature implies that the energy required per defect is initially decreased by defect interactions. At higher defect concentrations, additional repulsive interaction effects have been postulated[7] and only about 5–10% of the available anions can be displaced from their equilibrium sites.[2,8] The excess specific heat, which is indicated in Fig. 1,[9] shows that the maximum disordering rate probably occurs at about 1000 K, and the rate is not negligible at the melting point, 1146 K. The interactions responsible for limiting the defect concentration to 5–10% of the available anions could be either an additional energy requirement, a defect ordering tendency, or some combination of the two factors. Catlow and Hayes[10] have recently discussed this problem in terms of the formation of defect clusters, and this model would involve lowering both entropy and energy requirements.

The Faraday transition leads to very high anion mobilities,[11] but for $SrCl_2$, no experimental diffusion data have been reported for the superionic temperature range.[12] Nernst-Einstein calculations of the diffusion coefficients are subject to three major uncertainties: (1) a controversy on the magnitude of the electrical conductivity,[11] (2) correlation effects,[12] and (3) the suggestion that Frenkel defects might diffuse as associated pairs which are electrically neutral.[12] Diffusion coefficients calculated from the conductivity data of Carr *et al.*[13] attain values over 3×10^{-9} m^2/sec. These D values are about equal to those for fused salts and, since the maximum degree of disorder involves only approximately 5% of the available Cl^- sites, very high ionic mobilities are implied. High mobilities are required if an atomic diffusion mechanism is to make a detectable contribution to

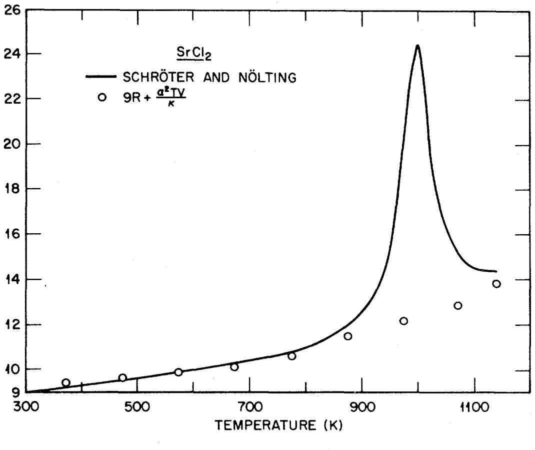

FIG. 1. The specific heat of $SrCl_2$ (Ref. 9). The base line, which assumes that the specific heat at constant volume is not sensitive to anharmonicities, was computed from the expansion coefficient α data of M. Shand and R. C. Hanson [Solid State Commun. 18, 769 (1976)], and compressibility K estimates based on the work of Cao-Xuan An [Phys. Status Solidi (a) 43, K69 (1977)].

the thermal conductivity.

Following the treatment of Price[2] yields a formula for the extra thermal conductivity λ^{xs}, and demonstrates the connection with the thermoelectric properties. The treatment assumes that vacancies and interstitials diffuse together, which would be expected if the superionic state involves formation of defect clusters.[10] Pair diffusion must occur in a statistical sense because, after the open circuit Seebeck emf E is set up, no further net transport of change occurs. The open circuit Seebeck emf, along with the concentration and temperature gradients, determine the equal steady-state drift velocities v of interstitials (i) and vacancies $(\square)$:

$$v_i = -\left[D_i \frac{d \ln C_i}{dT} + \frac{Q_i^* D_i}{RT^2} \right] \frac{dT}{dx} + \mu_i E \ , \tag{1}$$

$$v_\square = -\left[D_\square \frac{d \ln C_\square}{dT} + \frac{Q_\square^* D_\square}{RT^2} \right] \frac{dT}{dx} - \mu_\square E \ . \tag{2}$$

In these equations, the terms involving concentration C arise because the open circuit sample is in a temperature gradient and, as shown in Figs. 1 and 2, the defect concentration must therefore vary with position. The terms containing Q^* are the usual thermal diffusion factors which may be large compared to those for electrons and holes.

Expressing the mobilities μ in terms of diffusion coefficients and eliminating E leads to an expression for a steady-state flux of vacancy-interstitial pairs J_D, which involves the heats of transport Q^*:

$$J_D = -\frac{C_D D_i D_\square}{D_i + D_\square} \left[\frac{2 d \ln C_D}{dT} + \frac{Q_i^* + Q_\square^*}{RT^2} \right] \frac{dT}{dx} \ . \tag{3}$$

In (3), C_D is the defect (interstitial and vacancy) concentration in m^{-3}.

The extra thermal conductivity is then found by multiplying the defect flux by the energy per defect Q, which gives Fourier's first law:

$$J_Q = \lambda^{xs} \frac{dT}{dx} = Q J_D \ . \tag{4}$$

A more complete analysis based on the equations[14] for the fluxes of interstitials, vacancies, and energy gives a similar result but contains a contribution from the interstititial-vacancy drag which cannot be evaluated. This analysis shows that, in addition to the defect creation energy U, the energy transported also includes the heat of transport of the associated defect $(Q_i^* + Q^*)$: Thus,

$$\lambda^{xs} = \frac{C_D D_i D_\square}{D_i + D_\square} \left[\frac{2 d \ln C_D}{dT} + \frac{Q_i^* + Q_\square^*}{RT^2} \right] (U + Q_i^* + Q_\square^*) \ . \tag{5}$$

This is equivalent to the earlier equation for ambipolar thermodiffusion[2] but contains parameters more appropriate to ionic motion. The concentration gradient term is preserved in its general form because the concentration-temperature relationship for the defects cannot be expressed analytically in the temperature range of interest.

The formula [Eq. (5)] for λ^{xs} contains two types of terms: a driving force and energy which should be present in any high mobility material, and an added contribution from the temperature-dependent creation of vacancy-interstitial pairs. The latter contribution tends to disappear at higher temperatures because the rate of defect formation (Fig. 1) and energy for defect creation both should decrease. Ambipolar thermodiffusion (2) does not behave in this fashion and this point may have some practical significance. Bredig[15] has suggested that UO_2 also undergoes a Faraday transition and the high-temperature thermal conductivity of this material[16] has been discussed in terms of ambipolar thermodiffusion. The mechanism presented here leads to a different temperature variation.

A rigorous test of Eq. (5) is not possible at the present time. The experimental λ enhancement appears to about 0.05 to 0.1 W/mK in $SrCl_2$,[3] but the roles of parallel photon and phonon energy transport have not been resolved. This experimental problem is analogous to difficulties associated with identifying the ambipolar contribution to the thermal conductivity of Si.[17] An approximate upper limit for the predic-

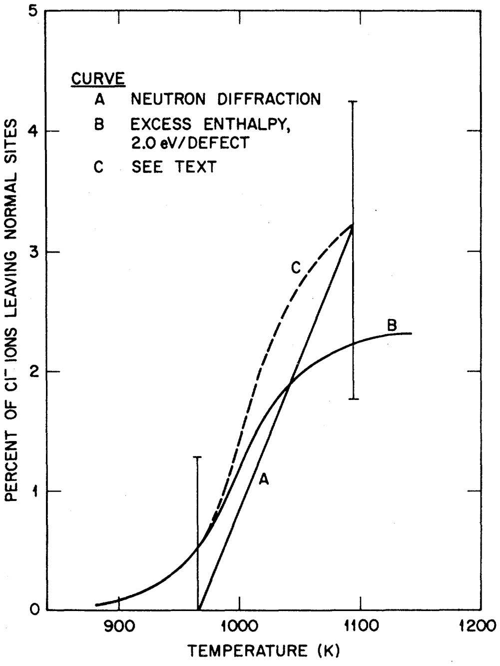

FIG. 2. Some estimates of the defect concentration in $SrCl_2$. The neutron-diffraction results are from Dickens *et al.* (Ref. 8) and the curve labeled B was calculated from the excess enthalpy data of Schröter and Nöting (Ref. 9) by assuming that the energy per event was 2.0 eV (Ref. 18).

tion [Eq. (5)] was established as follows:

(1) The D values for interstitials and vacancies were assumed to be equal and were calculated from the electrical conductivity data of Carr *et al.*[13]

(2) The defect concentration and its temperature dependence were obtained from the curve labeled "C" in Fig. 2. This curve was obtained by assuming that the energy of formation of an isolated defect is 2.0 eV,[18] and that this value decreases linearly with defect concentration.[7] Using the neutron-diffraction data to fix the defect concentration at 1100 K yields

$$h = 2.0 - 1.64 \times 10^{-27} C \ . \qquad (6)$$

The units in this equation are h in eV and C in m^{-3}. Forcing the integral of this equation to yield the excess enthalpy data[9] yields curve C. As shown in Fig. 2, this procedure could yield underestimates of both the defect concentration and its temperature dependence. This procedure [Eq. (6)] also defines the defect creation energy U, and it decreases by 60% at 1100 K. This change is larger than the one suggested by Catlow and Hayes.[10]

(3) The heat of transport $(Q_i^* + Q_\square^*)$ was estimated by using an equation[19] for the diffusional or convective thermal conductivity of a liquid. Eliminating $d\ln C_D/dT$ and U from Eq. (5) and equating the λ^{xs} result to the earlier formula[19] yields

$$Q_i^* + Q_\square^* = \left(\frac{12}{C_D V} \right)^{1/2} RT \ . \qquad (7)$$

The defect volume V was taken to be the ionic volume of Cl^- in the lattice and the specific heat of the defects was assumed to be $3R$ per mole. Larger Q^* values would be calculated if V were associated with the volume change for defect formation.[20] The result, ~2.7 eV per defect, is larger than expected from the theory of Wirtz[21] (≤ 1.2 eV) and values for fused salts[22] (0.2 eV). Thermoelectric data might help to resolve this point.

The result obtained by applying these assumptions to Eq. (5) is shown in Fig. 3. The calculation gives about 40% of the observed effect. Considering the many assumptions and the experimental uncertainty, this seems encouraging. This model could be tested further by making thermal conductivity measurements on other fast-ion conductors such as $\mathrm{PbF_2}$ or by studying $\mathrm{SrCl_2}$ with $\mathrm{GdCl_3}$ additions.[23] Adding $\mathrm{GdCl_3}$ should both enhance λ^{xs} because the electrical conductivity increases and suppress parallel conduction by phonons through point defect scattering.

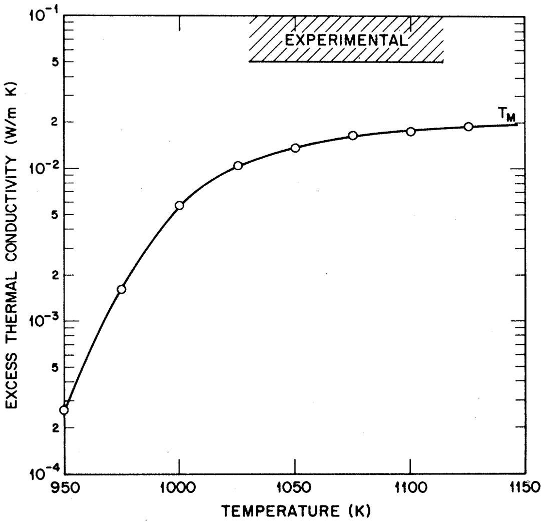

FIG. 3. Temperature dependence of the excess thermal conductivity of $\mathrm{SrCl_2}$.

ACKNOWLEDGMENTS

The author is indebted to J. P. Moore, D. L. McElroy, R. S. Graves, and F. J. Weaver for permission to use their results prior to publication. Discussions with Professor P. G. Klemens of the University of Connecticut were most helpful. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

---

[1] G. Slack, Solid State Phys. 34, 1 (1979).
[2] P. J. Price, Philos. Mag. 46, 1252 (1955).
[3] J. P. Moore, D. L. McElroy, R. S. Graves, and F. J. Weaver (unpublished).
[4] A. S. Dworkin and M. A. Bredig, J. Chem. Eng. Data 8, 416 (1963).
[5] M. J. Gillan and M. Dixon, J. Phys. C 13, 1901 (1980).
[6] M. Dixon and M. J. Gillan, J. Phys. C 13, 1919 (1980).
[7] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, and W. Hayes, J. Phys. C 11, 3197 (1978).
[8] M. H. Dickens, W. Hayes, M. T. Hutchings, and C. Smith, J. Phys. C 12, L97 (1979).
[9] W. Schröter and J. Nölting, J. Phys. (Paris) Colloq. 41, C6-20 (1980).
[10] C. R. A. Catlow and W. Hayes, J. Phys. C 15, L9 (1982).
[11] G. M. Hood and J. A. Morrison, J. Appl. Phys. 51, 3971 (1980).
[12] M. Beniere and M. Chemla, J. Phys. Chem. Solids 40, 729 (1979).
[13] V. M. Carr, A. V. Chadwick, and R. Saghafian, J. Phys. C 11, L637 (1978).
[14] P. H. Sutter, in *Thermoelectricity: Science and Engineering,* edited by R. R. Heikes and R. W. Ure (Interscience, New York, 1961), p. 154.

[15] M. A. Bredig, Colloq. Int. C.N.R.S. 205, 183 (1971).

[16] R. Brandt, G. Haufler, and G. Neuer, in *Thermal Conductivity and Emittance of Solid U0*$_2$, edited by Y. S. Touloukian, Center for Information and Numerical Data Analysis and Synthesis (Purdue University, West Lafayette, Ind., 1976).

[17] W. Fulkerson, J. P. Moore, R. K. Williams, R. S. Graves, and D. L. McElroy, Phys. Rev. 167, 765 (1968).

[18] P. J. Bendall, C. R. A. Catlow, and B. E. F. Fender, J. Phys. C 14, 4377 (1981).

[19] A. G. Turnbull, Aust. J. Appl. Sci. 12, 324 (1961).

[20] J. Oberschmidt and D. Lazarus, Phys. Rev. B 21, 2952 (1980).

[21] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill, New York, 1963), p. 191.

[22] A. Schiraldi and E. Pezzati, Z. Naturforsch. 33A, 42 (1978).

[23] C. R. A. Catlow, J. D. Comins, F. A. Germano, R. T. Harley, W. Hayes, and I. B. Owen, J. Phys. C 14, 329 (1981).