PHYSICAL REVIEW B VOLUME 22, NUMBER 12 15 DECEMBER 1980

Pressure and temperature dependences of the ionic conductivity of CsCl

G. A. Samara
Sandia National Laboratories, Albuquerque, New Mexico 87185*

(Received 31 July 1980)

Measurements of the pressure and temperature dependences of the ionic conductivity of CsCl combined with earlier diffusion and/or ionic conductivity measurements at atmospheric pressure have allowed determination of energies and volume relaxations associated with the formation and motion of Schottky defects in this crystal. An important result is that the lattice relaxation associated with vacancy formation is large and outward, the formation volume for Schottky pairs being 1.8–2.0 times the molar volume. The association energy of Cs^+ vacancies and divalent cation impurities is estimated to be 0.36 eV.

In this paper we present and discuss the effects of temperature and hydrostatic pressure on the ionic conductivity of cesium chloride (CsCl). The results have allowed determination of the energies and volume relaxations associated with the formation and motion of Schottky defects in this crystal. The association energy of Cs^+ vacancies and divalent cation impurities was also determined.

Earlier diffusion and/or ionic conductivity studies on CsCl at atmospheric pressure have led to the following conclusions[1,2]: (1) the conductivity is essentially completely ionic; (2) Schottky defects are dominant; (3) diffusive jumps are predominantly single vacancy near neighbor jumps, but with a small additional contribution from some more complex neutral species, possibly vacancy pairs; and (4) the mobility of the Cl^- ion vacancy is much larger than that of the Cs^+ ion vacancy.

There appear to be no earlier studies of the effects of pressure on ionic transport processes in CsCl.[3] In the study of ionic transport there is considerable interest in the investigation of the elastic relaxation of ions around defects. The determination of the activation volume for the formation and motion of lattice defects from pressure studies of diffusion and/or conductivity is one of the most direct means for studying this relaxation. Earlier pressure studies on alkali halides having the NaCl structure have shown that the relaxation of the lattice associated with vacancy formation is *outward* (i.e., the formation volume is larger than the molar volume).[4] This result has been in disagreement with theoretical calculations which show that the relaxation should be *inward* (i.e., the formation volume is smaller than the molar volume) for all models of ionic vacancies investigated.[5] This disagreement has not been understood. We thus felt it desirable to examine the situation for other ionic crystal types. This factor motivated our present pressure studies on CsCl and also on the thallous halides[6] all of which have the simple cubic CsCl structure.

The experimental details and data analysis are similar to those described earlier[6,7] and will not be repeated here. The ac conductivity measurements were made on CsCl samples cut from small single crystals obtained from the Harshaw Chemical Company (Solon, Ohio, U.S.A.). Measurements were made along one of the cubic axes (usually [100]).

Figure 1 shows the temperature dependence of the ionic conductivity, σ, expressed as $\log_{10}\sigma T$ vs $1/T$, at atmospheric pressure ($P=0$) and at 0.40 GPa (=4.0 kbars). Over the temperature range of the measurements the conductivity at atmospheric pressure exhibited two regimes. In regime I the conduction is known to be intrinsic, and our value of the activation energy $E_{\text{I}} = 1.33 \pm 0.02$ eV is in good agreement with earlier results.[1,2] Since the mobility of the Cl^- ion is known to be much higher than that of the Cs^+ ion, E_{I} is given by $E_{\text{I}} = \frac{1}{2}\Delta H_f + \Delta H_m^-$, where ΔH_f is the formation enthalpy for Schottky defects in CsCl and ΔH_m^- is the mobility enthalpy for the Cl^- ion. In regime II the conduction is extrinsic and the magnitude of σ is sample dependent. The $P=0$ data in Fig. 1 are on two samples which apparently have somewhat different impurity content. For both samples $E_{\text{II}} = 0.62 \pm 0.02$ eV, a value that is in good agreement with the enthalpy of motion for the Cs^+ vacancy (ΔH_m^+) in CsCl.[1,2] This is compatible with the presence of divalent (especially Ca) cation impurities in our samples. The enthalpy for Cl^- vacancy motion (ΔH_m^-) has been estimated to be of the order 0.2–0.3 eV.[1,2] For sample A1 in Fig. 1 we observed a third conduction regime (regime II′?) below 400 K at $P=0$ with $E \approx 0.19$ eV. This E may correspond to ΔH_m^-, but this is not certain. Using the value $\Delta H_m^- = 0.2-0.3$ eV with the above value of E_{I} in the intrinsic regime (1.33 eV) yields $\Delta H_f \simeq 2.1-2.3$ eV for the formation enthalpy of Schottky defects in CsCl. This compares favorably with ΔH_f's of 2.0 and 1.9 eV for CsBr and CsI, respectively.[1,2,8] Table I summarizes the ΔH's for CsCl.

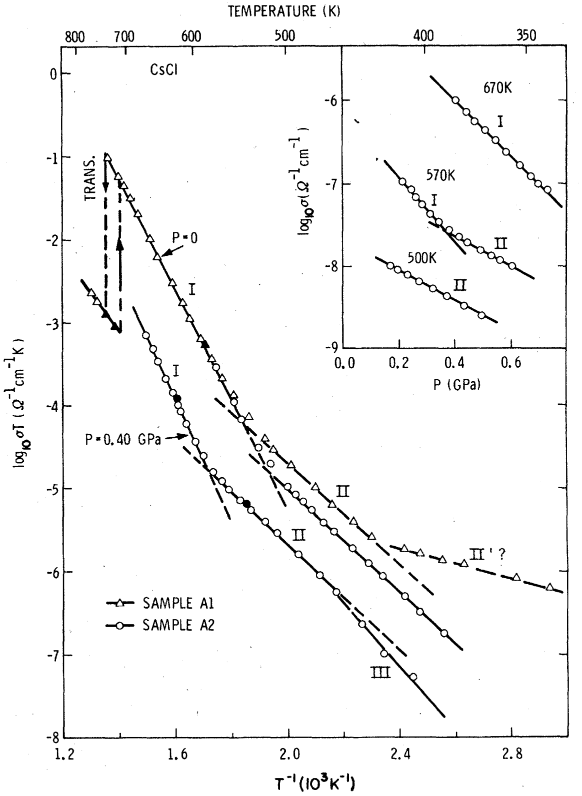

FIG. 1. Temperature dependence of the ionic conductivity of CsCl at 0 and 0.40 GPa showing the various conduction regimes. Also shown at atmospheric pressure is the change in conductivity at the structural transition to the NaCl structure. The inset shows the pressure dependence of the ionic conductivity at constant temperature in regimes I and II.

At atmospheric pressure CsCl transforms from the CsCl structure to the lower density NaCl structure at 740 K.[2] The transition is first order and is accompanied by a factor of 10^2 decrease in conductivity (Fig. 1). Since pressure favors the CsCl phase the transition temperature is expected to increase with pressure. We did not investigate the pressure dependence of this transition because the expected increase in transition temperature placed the latter outside the range of the apparatus used.

Pressure causes a large suppression of the conductivity as shown in Fig. 1. This is associated with increases in the activation energies with pressure. Measurements at different pressures up to 8 kbars yielded $dE_I/dP = (37.5 \pm 1.5) \times 10^{-2}$ eV/GPa and $dE_{II}/dP = (7 \pm 2) \times 10^{-2}$ eV/GPa. The large increase in E_I with pressure is due mainly to the increase in Schottky-defect-formation enthalpy. Note that the 0.4 GPa isobar in Fig. 1 exhibits a third conduction regime (III) in which σ decreases with decreasing T faster than it does in regime II. Regime III was observed in several isobars and we believe that it is due to association of Cs$^+$ vacancies and divalent cation impurities to form neutral bound pairs which do not contribute to the conductivity. On this basis and from the activation energy in regime III ($E_{III} \simeq 0.80$ eV) we estimate this association energy to be $\Delta H_a \simeq 0.36$ eV from the expression $E_{III} = \frac{1}{2}\Delta H_a + \Delta H_m^+$. This appears to be the first evaluation of this quantity in CsCl.

At constant T, $\log_{10}\sigma$ decreases linearly with pressure. This is illustrated in the inset in Fig. 1. The 500- and 670-K data correspond to the pressure dependences of σ in the extrinsic (II) and extrinsic (I) regimes, respectively, whereas the 570-K data show the pressure-induced transition from intrinsic (regime I) to extrinsic conduction (regime II). From the measured pressure dependences of σ as determined from both σ vs P isotherms and σ vs T isobars we can calculate the activation volumes, ΔV, for regimes I and II from the expression[4,6,7]

$$\Delta V = -kT\left[\left(\frac{\partial \ln\sigma}{\partial P}\right)_T - \left(\frac{\partial \ln N}{\partial P}\right)_T - \left(\frac{\partial \ln\nu}{\partial P}\right)_T - 2\left(\frac{\partial \ln r}{\partial P}\right)_T\right]. \qquad (1)$$

In Eq. (1) N is the number of ions (sites) per unit volume, ν is the vibrational (or attempt) frequency of the mobile species in the direction which carries it over the energy barrier, and r is the jump

TABLE I. Values of the enthalpies, ΔH, and activation volumes, ΔV, for the motion and formation of Schottky defects in CsCl. The ratio of the formation volume to the molar volume ($\Delta V_f/V_M$) is also given. The ΔV's are nearly temperature independent.

	ΔH (eV)	ΔV (cm^3/mole)	$\Delta V_f/V_M$
Motion of Cs$^+$ vacancies	0.62 ± 0.02	18.0 ± 2.0	
Motion of Cl$^-$ vacancies	0.2–0.3[a]	5.5–9.0	
Formation of Schottky pairs	2.1–2.3[b]	80–87	1.8–2.0

[a] Estimated range taken from Ref. 2.
[b] See text.

distance. From the known values of the isothermal compressibility[9] and Grüneisen parameter[10] of CsCl, and following earlier procedures,[6,7] we obtain the activation volumes shown in Fig. 2. These volumes are nearly temperature independent over the temperature ranges covered. The width of the shaded bands of ΔV values in Fig. 2 represents the estimated uncertainties in the various quantities in Eq. (1).

The calculated ΔV's in regime II simply represent the motional activation volumes for the Cs^+ vacancy (ΔV_m^+) since transport in this regime is dominated by the mobility of this vacancy.[1,2] In regime *I* the conductivity is intrinsic and dominated by the mobility of the Cl^- vacancies so that the calculated ΔV's represent [6,7] $(\frac{1}{2}\Delta V_f + \Delta V_m^-)$, where ΔV_f is the formation volume for Schottky pairs and ΔV_m^- is the motional activation volume for Cl^- vacancies.

To obtain ΔV_f we need to know ΔV_m^-. Unfortunately, the available samples did not allow us to measure inequivocally $\sigma(P)$ in an extrinsic regime where the motion of the Cl^- vacancy was dominant. Thus we do not have a direct measure of ΔV_m^-. However, we can estimate ΔV_m^- in the following way. Flynn[11] has presented a dynamical theory of diffusion which leads to the prediction that

$$\Delta V_m^-/\Delta V_m^+ = \Delta G_m^-/\Delta G_m^+ . \qquad (2)$$

The known values of ΔV_m^+ and the $\Delta G^\pm$'s for CsCl lead to the conclusion that $\Delta V_m^- = 5.5 - 9.0$ cm^3/mole, the spread being largely due to the spread in ΔH_m^- which is estimated to fall in the range 0.2 – 0.3 eV. This range of ΔV_m^-'s leads to $\Delta V_f = 80 - 87$ cm^3/mole. The activation volumes are summarized in Table I.

The most important feature of the results in Table I is the large value of the formation volume (ΔV_f) for Schottky defects in CsCl. This value is about 80 – 100% *larger* than the molar volume V_M. One can very readily confirm that this conclusion is not materially affected by any realistic uncertainties in the estimated value of ΔV_m^- discussed above. We have recently found a qualitatively similar result (i.e., $\Delta V_f > V_M$) for the two crystals TlCl and TlBr which have the CsCl structure.[3,6] Thus the relaxation of the lattice associated with vacancy formation for these CsCl-type materials is *outward* as is true of alkali halides having the NaCl structure.[4,5] These results are in *qualitative* disagreement with conclusions deduced from earlier detailed model calculations on the NaCl structure which yielded *inward* volume relaxation.[5] The model calculations indicate that the inward relaxation is a general consequence of *all* models of ionic vacancies and is a manifestation of the long range of the Coulomb field of the vacancy acting on the ions of the lattice coupled with the also slow decrease in induced moments with distance.[5]

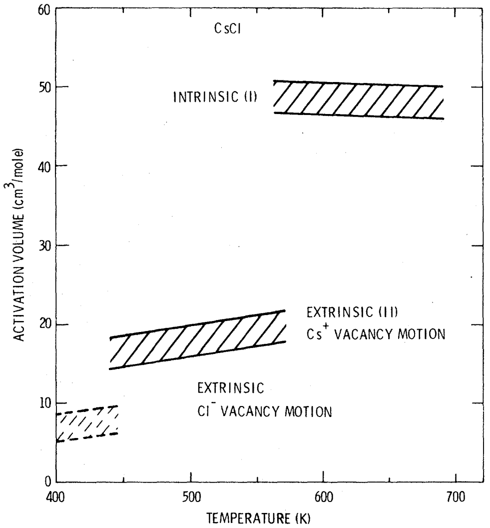

FIG. 2. Activation volume of CsCl in the intrinsic (I) regime and in the extrinsic (II) regime dominated by Cs^+ vacancy motion. Also depicted (dashed lines) is the estimated activation volume for Cl^- vacancy motion. The width of the shaded bands represents the estimated uncertainties.

Two very recent model calculations appear to have resolved the above discrepancy between theory and experiments. Both calculations yield *outward* volume relaxation on vacancy formation in agreement with the experimental results. Although the calculations were specifically performed on the NaCl structure, they are expected to hold for other ionic crystal types. In one of these calculations Lidiard[12] added a correction to the earlier lattice statics calculations[5] of ΔV_f. The need for this correction arises because the earlier calculations assumed that the force constants which describe the distorted lattice around the vacancy were independent of volume. The correction removes this assumption and this in turn leads to an additional positive ΔV which makes $\Delta V_f > V_M$, as required.

In the second calculation Gillan[13] uses the so-called volume derivative method to calculate ΔV_f. This method, which implicitly includes anharmonic contributions neglected in earlier treatments, makes use of the relation between ΔV_f and the derivative with respect to volume of the energy of formation. The latter is obtained from detailed computer calculations in which the initial positions of the ions are specified, and the ions are allowed to interact through specified interionic potentials. The system is then allowed to relax to the configuration of minimum energy.

Finally, reference to Table I shows that ΔH_m and

ΔV_m for Cl^- vacancies are considerably smaller than the corresponding values for Cs^+ vacancies. Two factors contribute to this difference. First, the polarizability of the Cs^+ ion is larger than that of the Cl^- ion (3.34 Å^3 vs 2.96 Å^3),[14] and it is known that the polarization contributes a positive term to ΔH_m, and thereby also to ΔV_m.[11] Second, the Cl^- ion is larger than the Cs^+ ion (1.81 Å vs 1.69 Å in radius). Reference to the CsCl structure shows that this size difference allows less space for near-neighbor Cs^+ ion jumps than it does for near-neighbor Cl^- ion jumps, and this leads to larger ΔH_m and ΔV_m for Cs^+ ion motion.

It is a pleasure to acknowledge the expert technical assistance of B. E. Hammons. I also thank Dr. A. B. Lidiard and Dr. M. J. Gillan for sending copies of their forthcoming papers prior to publication. This work was sponsored by the U. S. Department of Energy under Contract No. DE-AC04-76-DP00789.

---

*A facility of the U.S. Dept. of Energy.

[1] P. J. Harvey and I. M. Hoodless, Philos. Mag. 16, 543 (1967).

[2] J. Arends and H. Nijboer, Solid State Commun. 5, 163 (1967).

[3] A brief account of the present results has been recently given elsewhere; G. A. Samara, Phys. Rev. Lett. 44, 670 (1980).

[4] M. Beyeler and D. Lazarus, Z. Naturforsch. 26a, 291 (1971); D. N. Yoon and D. Lazarus, Phys. Rev. B 5, 4935 (1972) and references therein.

[5] I. D. Faux and A. B. Lidiard, Z. Naturforsch. 26a, 62 (1971) and references therein. See Refs. 12 and 13 below for new results which remove the discrepancy between theory and experiments. These results were sent to us by the authors after the completion of the present experimental work.

[6] G. A. Samara (unpublished).

[7] G. A. Samara, J. Phys. Chem. Solids 40, 509 (1979).

[8] D. W. Lynch, Phys. Rev. 118, 468 (1960).

[9] H. G. Drickamer, R. W. Lynch, R. L. Clendenen, and E. A. Perez-Albuerne, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 19, p. 140.

[10] A. C. Bailey and B. Yates, Philos. Mag. 16, 1241 (1967).

[11] C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972) Chaps. 7, 9, and 12.

[12] A. B. Lidiard (unpublished).

[13] M. J. Gillan (unpublished).

[14] J. R. Tessman, A. H. Kahn, and W. Shockley. Phys. Rev. 92, 890 (1953).