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## Elastic Relaxation Associated with the Formation and Motion of Schottky Defects in Ionic Crystals

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Present results on CsCl-type and earlier work on NaCl-type solid ionic conductors have indicated that the relaxation of the lattice associated with vacancy formation is outward (i.e., the formation volume is greater than the molar volume). This is in qualitative disagreement with available theoretical calculations which show that the relaxation should be inward for all models of ionic vacancies investigated.

Studies of the combined effects of hydrostatic pressure and temperature on the ionic conductivities of the thallos halides (TlCl and TlBr) and of caesium chloride (CsCl) have allowed determination of the lattice volume relaxations and energies associated with the formation and motion of Schottky defects in these crystals. A particularly important result reported in this Letter is the finding that for these CsCl-type crystals the relaxation of the lattice associated with vacancy formation is *outward* (i.e., the formation volume is greater than the molar volume). While this appears to be the first such result on any crystals having the CsCl structure, earlier studies<sup>1,2</sup> on ionic crystals having the NaCl structure have yielded a similar result. This *outward* relaxation thus appears to be a general result for ionic crystals of both the NaCl and CsCl types (and probably of other ionic lattice types), and it is in qualitative disagreement with theoretical calculations which show that the relaxation should be *inward* (i.e., the formation volume is less than the

molar volume) for all models of ionic vacancies investigated.<sup>1</sup> Resolution of this discrepancy is very important since it relates directly to our understanding of the nature of forces in simple ionic crystals.

There is considerable interest in the investigation of the 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 ionic conductivity is one of the most direct means for studying this relaxation.<sup>1,2</sup> For the NaCl structure all model calculations that have been done predict an *inward* lattice relaxation for vacancies, whereas pressure results (on alkali halides) yield a relatively large *outward* relaxation.<sup>1,2</sup> This disagreement is not understood. It is of much interest to examine the situation for other ionic crystal types. This interest motivated the present work on the CsCl structure. There has been relatively little work on ionic transport and the defect nature in ionic crystals having the CsCl structure

compared, say, to crystals having the NaCl structure, and in particular, we are not aware of any earlier pressure studies on CsCl-type crystals.

Earlier diffusion and/or ionic conductivity studies on TlCl,<sup>3</sup> TlBr,<sup>4</sup> and CsCl<sup>5</sup> have led to the following conclusions: (1) The conductivity is strictly ionic. (2) Schottky defects are predominant. (3) Diffusive jumps are predominantly near-neighbor jumps. (4) The mobility of the anion vacancy is much larger than that of the cation vacancy. (5) For TlCl and TlBr the intrinsic conductivity is sufficiently high and polyvalent dopants are not sufficiently soluble so as to give separable extrinsic regimes. Thus, there is no information from conductivity data on the formation and motion energies of the individual defects in these two crystals. However, we have found that pressure suppresses the intrinsic conductivity and makes it possible to observe extrinsic conduction.<sup>6</sup>

The present measurements were made on single-crystal samples. The samples were nominally pure; however, chemical analyses revealed a variety of monovalent and polyvalent impurities.<sup>6</sup> Details of the measurement techniques and apparatus can be found elsewhere.<sup>7</sup> Before presenting and discussing the results it is helpful to recall some basic considerations. The conductivity is given by the familiar expression<sup>7</sup>

$$\sigma T = \left( \frac{ANq^2\nu r^2}{k} \right) \exp\left( -\frac{\Delta G_f}{2kT} - \frac{\Delta G_m}{kT} \right) \quad (1a)$$

$$= \left( \frac{ANq^2\nu r^2}{k} \right) \exp\left( \frac{\Delta S_f}{2k} + \frac{\Delta S_m}{k} \right) \times \exp\left[ -\left( \frac{\Delta H_f}{2kT} - \frac{\Delta H_m}{kT} \right) \right], \quad (1b)$$

where  $A$  is a constant which depends on the lattice type,  $N$  is the density of carriers,  $q$  is the charge,  $\nu$  is the attempt frequency, and  $r$  is a

jump distance. The  $\Delta G$ 's are the Gibbs free energies associated with the formation ( $f$ ) and motion ( $m$ ) of the defects; they can be written in terms of the corresponding entropies,  $\Delta S$ , and enthalpies,  $\Delta H$ , as shown. Equation (1) is generally written in terms of a preexponential  $\sigma_0$  and an activation energy  $E$ , i.e.,  $\sigma T = \sigma_0 \exp(-E/kT)$ . Referring to Eqs. (1) we note that in the intrinsic regime  $E$  is equal to one-half of the formation energy for the defect (Schottky pairs in the present case) plus the mobility enthalpy (where one mobile species dominates), i.e.,  $E = \frac{1}{2}\Delta H_f + \Delta H_m$ . In the extrinsic regime, on the other hand,  $E$  is simply the motional enthalpy of the dominant species, i.e.,  $E = \Delta H_m$ .

The activation volume, which may be viewed as the contribution of the defects and mobile species to the volume of the crystal,<sup>8</sup> is given by the thermodynamic identity  $\Delta V = (\partial \Delta G / \partial P)_T$ . Reference to Eq. (1a) shows that  $\Delta V$  can be readily evaluated from the pressure dependences of  $\sigma$  and some of the terms in the preexponential, namely

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

The pressure dependence of  $\sigma$  is by far the dominant contribution to  $\Delta V$ ,<sup>2,7</sup> but nevertheless the other contributions were taken into consideration in the present work.<sup>6</sup> Note that in the intrinsic regime  $\Delta V = \frac{1}{2}\Delta V_f + \Delta V_m$ , whereas in the extrinsic regime  $\Delta V = \Delta V_m$ .

Now I present some of the results and their interpretation. At atmospheric pressure ( $P=0$ ) and for temperatures in the range 350–700 K the conduction is intrinsic for both TlCl and TlBr. However, at high pressure both intrinsic and well-defined extrinsic regimes were observed.<sup>6</sup> Measurements on samples with different trace

TABLE I. Values of the enthalpies ( $\Delta H$  in electronvolts) and activation volumes ( $\Delta V$  in cubic centimeters per mole) for the motion (subscript  $m$ ) of positive and negative ion vacancies as well as for the formation (subscript  $f$ ) of Schottky defects in TlCl, TlBr, and CsCl. The uncertainties in  $\Delta V_f$  are estimated to be  $< \pm 10\%$ . Also given is the ratio of  $\Delta V_f$  to the molar volume  $V_M$  at 500 K.

Crystal	$\Delta H_m^+$	$\Delta H_m^-$	$\Delta H_f$	$\Delta V_m^+$	$\Delta V_m^-$	$\Delta V_f$	$\Delta V_f/V_M$
TlCl	0.50	0.11	1.36	16.1	4.8	41.0	1.16
TlBr	0.56	~0.25	1.10	13.7	6.8	44.4	1.14
CsCl	0.62	0.2–0.3 <sup>a</sup>	2.1–2.3	18.0	5.5–9.0	80–87	1.8–2.0

<sup>a</sup> Estimated range taken from Ref. 5.

impurities combined with earlier data<sup>3,4,9</sup> have allowed an evaluation of both the cation and anion motional enthalpies ( $\Delta H_m^+$  and  $\Delta H_m^-$ , respectively) as well as the formation enthalpies ( $\Delta H_f$ ) for Schottky pairs for both crystals.<sup>6</sup> The results are summarized in Table I. The TlCl results are in generally good agreement with  $\Delta H$  values determined from diffusion and thermoelectric power measurements.<sup>3,9</sup> Apparently there are no earlier data on TlBr to compare the present results with.

Table I also shows the activation volumes for cation and anion motion and for the formation of Schottky pairs in TlBr and TlCl. These  $\Delta V$ 's were evaluated from low-pressure ( $\leq 0.4$  GPa)  $\sigma(P)$  data via Eq. (2). In each conduction regime  $\ln\sigma$  was found to decrease linearly with pressure at low pressures. Note that the  $\Delta V$ 's show only a weak temperature dependence. Also note from Table I that the motional volumes for the  $\text{Tl}^+$  ion are considerably larger than those for the  $\text{Br}^-$  and  $\text{Cl}^-$  ions as is true of the motional enthalpies. This is most likely due to the larger polarizability of the  $\text{Tl}^+$  ion.

In the case of CsCl the conductivity at atmospheric pressure exhibited two regimes, an intrinsic regime (I) with  $E_I = 1.33 \pm 0.02$  eV and an extrinsic regime (II) with  $E_{II} = 0.62 \pm 0.02$  eV which is dominated by the motion of the  $\text{Cs}^+$  ions. Both  $E$ 's are in good agreement with earlier work.<sup>5</sup> Table I summarizes the  $\Delta H$ 's. Pressure suppresses the conductivity of CsCl in both regimes, and there are corresponding increases in  $E_I$  and  $E_{II}$  as is true for TlCl and TlBr. From the pressure derivatives of  $\sigma$  I calculate the activation volumes given in Table I. These results require some comment. The motional activation volume for the  $\text{Cs}^+$  vacancy ( $\Delta V_m^+$ ) was deduced directly from the  $\sigma(P)$  data in regime II. Similarly the  $\sigma(P)$  data in regime I yielded  $\Delta V = 49.0$  cm<sup>3</sup>/mole ( $= \frac{1}{2}\Delta V_f + \Delta V_m^-$ ), because conduction in this intrinsic regime is dominated by the mobility of the  $\text{Cl}^-$  vacancy. To obtain  $\Delta V_f$  we need to know  $\Delta V_m^-$ . Unfortunately, the available samples did not allow me to measure  $\sigma(P)$  in an extrinsic regime where the motion of the  $\text{Cl}^-$  vacancy was dominant. However, one can estimate  $\Delta V_m^-$  in the following way. Flynn<sup>10</sup> has presented a dynamical theory of diffusion which leads to the prediction that  $\Delta V_m^- / \Delta V_m^+ = \Delta G_m^- / \Delta G_m^+$ . The known values of  $\Delta V_m^+$  and the  $\Delta G^\ddagger$ 's for CsCl lead to the conclusion that  $\Delta V_m^- = 5.5$ – $9.0$  cm<sup>3</sup>/mole, the spread being largely due to the spread in  $\Delta H_m^-$ . This range of  $\Delta V_m^-$ 's leads to  $\Delta V_f = 80$ – $87$  cm<sup>3</sup>/

mole. These values are summarized in Table I.

For the purposes of this Letter, the most important feature of the results in Table I for TlCl, TlBr, and CsCl is the large value of the formation volume ( $\Delta V_f$ ) for Schottky defects in these crystals. This value is  $\sim 15\%$  larger than the molar volume  $V_M$  for both TlCl and TlBr, and it is about 80–100% larger than  $V_M$  for CsCl. One can very readily confirm that for the latter crystal this conclusion is not materially affected by any realistic uncertainties in the estimated value of  $\Delta V_m^-$  discussed above. Thus for the three crystals TlCl, TlBr, and CsCl, which have the CsCl structure, the relaxation of the lattice associated with vacancy formation is *outward* as is true of alkali halides having the NaCl structure.<sup>1,2</sup> By way of comparison, earlier results on NaCl-type crystals have yielded  $\Delta V_f/V_M$  (at  $\sim 970$  K) values of 1.9, 1.5, 1.2, and 1.1 for NaCl, KCl, NaBr, and KBr, respectively.<sup>2</sup> As noted earlier, detailed model calculations on the NaCl structure<sup>1</sup> yield inward volume relaxation, in qualitative disagreement with the conclusion deduced from the pressure results. 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.<sup>1</sup> Thus the discrepancy between theory and experiment obtains for both the NaCl and CsCl structures and possibly for other ionic structure types. This discrepancy is quite fundamental and deserves serious attention.

Faux and Lidiard<sup>1</sup> have raised the possibility that anharmonic lattice effects may be responsible for the above discrepancy. Specifically, the models calculate  $\Delta V_f$  in the harmonic approximation, whereas experimentally  $\Delta V_f$  is deduced from high-temperature data where anharmonic effects may be important. What would be needed to resolve the discrepancy is a  $\Delta V_f$  that increases with  $T$  as anharmonic interactions become stronger. While this proposition is tempting, the large magnitude of the discrepancy, especially for NaCl, KCl, and CsCl, makes it extremely unlikely that this is the explanation.<sup>2</sup> Perhaps more importantly, there are two observations which essentially rule out this explanation. They are that (1) the most highly anharmonic crystals (TlCl and TlBr, Ref. 11) among all the crystals that have been investigated show about the smallest discrepancy, and (2) the alkali bromides,

whose lattices are more anharmonic than the chlorides, exhibit much smaller discrepancies than the chlorides.

Finally, it should be emphasized that Eq. (1), and thereby Eq. (2), are based on the absolute rate theory.<sup>8</sup> Implicit in this theory is the assumption that the diffusive process can be described in terms of equilibrium statistical mechanics. Although there has been some criticism of this theory, it nevertheless has been very successful in treating diffusion and ionic conduction, and this success is generally taken as the strongest evidence for its validity.<sup>8</sup>

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## New Mechanism for Resonant Photoemission

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We present a mechanism for the resonance near the  $3p$  threshold in the photoemission associated with the two-hole bound state in metals such as Cu and Zn. It is based upon the strong interaction between the  $4s$ - $4p$  conduction-band electrons and the two bound holes (the  $3d^8$  configuration) resulting from the super Coster-Kronig decay of the  $3p$  core hole. This effect also occurs in Ni but is not dominant.

This Letter reports a new mechanism for resonant photoemission resulting from the super Coster-Kronig decay<sup>1</sup> of a  $3p$  core hole ( $3p^5 3d^{10} \rightarrow 3p^6 3d^8 \epsilon l$ ). Unlike the model described by Penn,<sup>2</sup> this mechanism is operative in metals with filled  $3d$  bands such as Cu and Zn. It is based upon the strong interaction between the  $4s$ - $4p$  conduction-band electrons and the two bound holes (the  $3d^8$  configuration) produced in the final state. Our calculations clearly exhibit a resonance in the  $3d^8$  satellite at fixed binding energy and the appearance above resonance of a separate, "Auger" peak at fixed kinetic energy.

Resonant photoemission in Ni metal was discovered by Guillot *et al.*<sup>3</sup> They observed that, for photon energy  $h\nu$  near the  $3p$  threshold (66 eV), the emission from the 6-eV satellite associated with the  $3d$  valence band was greatly enhanced.

Iwan, Himpfel, and Eastman<sup>4</sup> observed a similar, although weaker, resonance in Cu. They anticipate that such a resonance is a common feature of the row Cu, Zn, . . . , because atomic effects are important in their respective Auger spectra.<sup>5</sup> Since the Penn model gives no resonance when the  $3d$  bands are filled, it fails to explain the data in Cu. The presence of a satellite in Cu does not invalidate the Penn model for Ni, however. The mechanism proposed here is an additional effect which is probably dominant only in Cu, Zn, etc.

For simplicity, we consider only a single conduction band (analogous to the  $4s$ - $4p$  bands) into which the core electron is excited when a photon is absorbed. The Hamiltonian for this model has been described by Nozières and de Dominicis<sup>6</sup> for the x-ray edge problem. In the initial (ground)