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DEFECTS IN IONIC SOLIDS WITH CsCl STRUCTURE

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Résumé. — Le calcul des énergies de formation de lacunes isolées dans une famille de cristaux de type CsCl (halogénures de césium, thallium et ammonium) est réexaminé par une approche de minimisation de l'énergie. Un accroissement de la relaxation et une diminution du moment électrique des ions plus proches voisins ont conduit à des valeurs de l'énergie de formation de défaut de Schottky supérieures aux résultats antérieurs ⁽¹⁾. La comparaison aux études de conductivité et de diffusion suggère que les propriétés de transport dans les halogénures de césium et de thallium sont dues à un mécanisme lacunaire.

Nous avons effectué des mesures de la conductivité électrique et des pertes diélectriques dans des cristaux de NH_4Cl dopé par Co^{++} . Les pics de perte diélectrique peuvent être attribués à la réorientation des dipôles impureté interstitielle-lacune. Pour une impureté associée, les fréquences du pic de perte sont déterminées par les sauts de la lacune en premier voisin.

Abstract. — The energetics of formation of isolated vacancies in a family of CsCl type crystals (the halides of caesium, thallium and ammonium) are reexamined by using an energy minimisation approach. An increased relaxation and decreased electronic moment of the nearest neighbour ions resulted in overall energy terms leading to values of Schottky defect formation energies which are consistently larger relative to the previous results ⁽¹⁾. Comparison with ionic conductivity and diffusion studies suggests that the transport properties in caesium and thallous halides may be understood in terms of Schottky defect mechanisms.

We have made measurements on the electrical conductivity and dielectric loss of Co^{++} doped NH_4Cl crystals. The observed dielectric loss peaks can be attributed to the reorientation of interstitial impurity-vacancy type dipoles. For a single bound vacancy the loss peak frequencies are determined by the first neighbour vacancy jumps. These results suggest that a vacancy charge transport mechanism cannot be ruled out in the ammonium halides.

1. Theoretical calculation of Schottky defect energies.

— Schottky defect formation energies in the family of seven crystals with CsCl structure (CsCl , CsBr , CsI , TlCl , TlBr , NH_4Cl and NH_4Br) have been previously calculated by us using the force balance method in the Mott-Littleton model (Murthy and Murti 1971). The computed formation energies have generally been compatible with available experimental values. We have since reexamined the energetics of the formation of Schottky defects in these crystals by applying the more general approach of minimising the energy of the defect solid. The energy minimisation conditions can be seen to contain extra force terms arising from the interaction of regions I and II in addition to the terms occurring in the usual force balance procedure. Although these terms appear to be of small magnitude, it is not clear to what extent they influence the equilibrium configuration of region I. Adopting the Boswarva and Lidiard (1967) and Boswarva (1967) formulation, we have obtained the equilibrium relaxations of the nearest neighbours which remain positive and larger than in the force balance calculation.

⁽¹⁾ Murthy, C. S. N. and Murti, Y. V. G. S., *J. Phys. C*, **4** (1971) 1108.

We have compared the electrostatic (F_e) and short range forces (F_R) of the force balance method and those implicit in the energy minimisation procedure. These forces are deduced from the various energy terms by numerically differentiating the calculated energies. We notice the following interesting points from such a comparison : 1) The short range force is altered very little thereby indicating that the additional interactions terms arising between the first and second regions ions are negligible. 2) The electrostatic force is enhanced considerably resulting in a large outward displacement. An examination of the electrostatic terms in both the procedures reveals that the effective Coulombic interaction in the case of energy minimisation procedure consists of additional terms originating from the change in the polarisation energy of region I upon relaxation as well as the polarisation interaction between regions I and II (E_5) in excess of the polarisation resulting from the vacancy field. Thus the first five terms of F_e (Murthy and Murti 1971) due to the effective charge of the defect and the displacement of the other region I ions are explicitly taken care of by ΔE_c^I (change in Coulombic energy of region I) in the energy minimisation procedure whereas the effect to electronic

dipole moment of the seven ions is considered in E_5 in an implicit manner. Since we deduced the forces from the energy terms, the combined effect of the electronic and displacement dipoles of region II ions obtained from the polarisation and relaxation energy (E_4) of region II, is reduced by half of its amount in comparison with the corresponding force balance value. The expressions E_i are as given in Boswarva (1967). Thus the total electrostatic force is increased while the repulsion force is practically unchanged so that the equilibrium relaxations are enhanced. Since the electronic dipole moment of region I ions depends also on the ion displacements the larger outward relaxation results in a decrease of the dipole moments. The overall result of the decreased moments and raised displacements is an enhancement of the h_s values. The results are displayed in table I.

2. Experimental studies in NH_4Cl crystals. —

The electrical conductivity of nominally pure NH_4Cl single crystals in the temperature range 85°C to 175 °C is given by the equation

$$\sigma T = 1.29 \times 10^9 \exp(-1.22 \text{ eV}/kT) \Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{K}.$$

with a rather limited range of impurity controlled conduction.

Two additional regions are observed in Co-doped crystals (0.047 to 0.258 mole percent) subjected to several hours of the thermal cycling. The conductivity in the region II (occurring below the intrinsic region) is typically given by

$$\sigma T = 5.95 \times 10^4 \exp(-0.877 \text{ eV}/kT) \Omega^{-1} \cdot \text{cm}^{-1} \cdot \text{K}.$$

The third region of conductivity at still lower temperatures has an activation energy of 0.27 eV (Fig. 1).

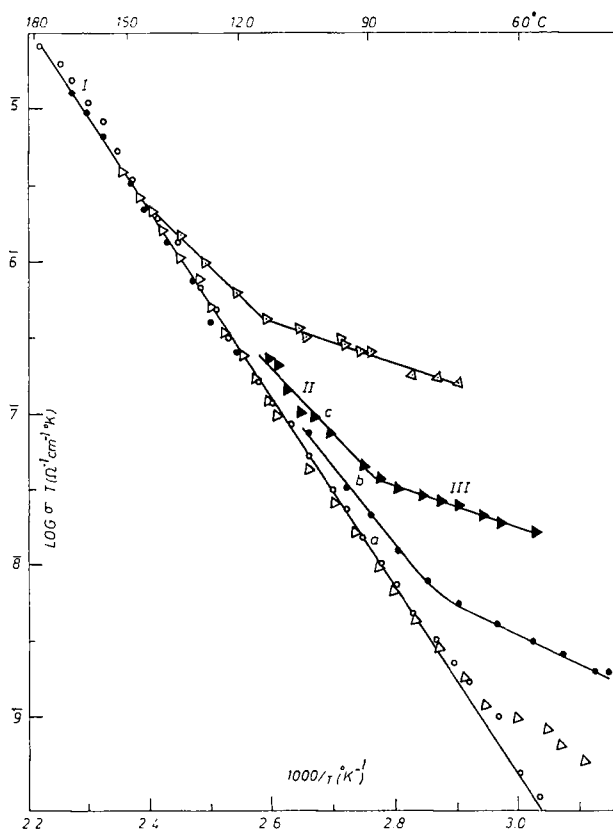


FIG. 1.

The doped crystals exhibit isothermal dielectric loss peaks in the audio frequency range between 60 °C to 90 °C. The shift of the peak positions with temperatures leads to an activation energy of 0.61 eV which represents the activation energy for re-orientation of the dipoles (Fig. 3).

TABLE I

Schottky defect energy parameters. Energy minimisation procedure

Crystal	Vacancy	ζ in units of r		m in units of er		W_{\pm} (eV)	h_s (eV)
CsCl (*)	Cation	0.057	(0.062)	0.021	(0.019)	4.460 (4.309)	1.986 (1.998)
	Anion	0.060	(0.053)	0.023	(0.025)	4.353 (4.516)	
CsBr (*)	Cation	0.053	(0.058)	0.027	(0.026)	4.300 (4.187)	1.878 (1.940)
	Anion	0.062	(0.054)	0.019	(0.021)	4.153 (4.328)	
CsI (*)	Cation	0.060	(0.064)	0.034	(0.033)	4.044 (3.926)	1.517 (1.613)
	Anion	0.080	(0.067)	0.013	(0.015)	3.809 (4.025)	
TiCl	Cation	0.055		0.021		4.863	1.349
	Anion	0.086		0.025		3.948	
TiBr	Cation	0.050		0.028		4.821	1.322
	Anion	0.090		0.020		3.792	
NH_4Cl	Cation	0.069		0.022		4.373	1.387
	Anion	0.086		0.011		3.982	
NH_4Br	Cation	0.067		0.027		4.200	1.239
	Anion	0.092		0.008		3.711	

(*) Values in parenthesis are for the Tosi-Fumi radii corrected to the CsCl structure.

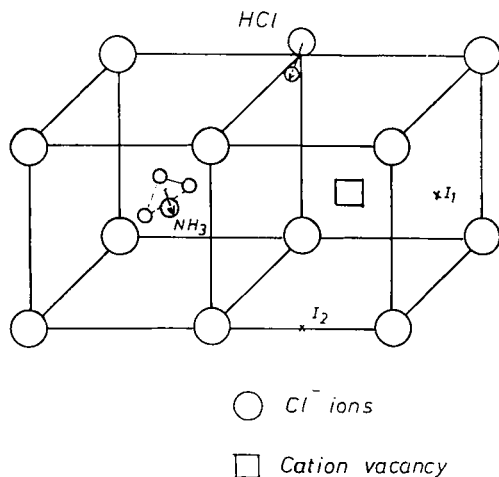


FIG. 2.

There is considerable evidence from electron spin resonance (Zaripov and Chirikin 1965, Pilbrow and Spaeth 1967, Sastry and Venkateswarlu 1967) and optical absorption (Goode 1965, Narayana and Venkateswarlu 1970, 1971) studies that divalent transition metal ions like Mn^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} take up interstitial positions in the lattice of NH_4Cl . The two possible interstitial sites of the impurity with respect to a Cs^+ ion at (000) are (Fig. 2): $1^0 I_1$ at $(\frac{1}{2}00)$ type sites at the centre of four Cl^- ions in $\{100\}$ planes and $2^0 I_2$ at $(\frac{1}{2}\frac{1}{2}0)$ type sites between two Cl^- ions. For the I_2 site the Coulomb energy is negative favouring this site for impurity ions of small size. We propose that out of the two vacancies required for charge compensation, one vacancy is bound to the impurity in a first neighbour site while the second

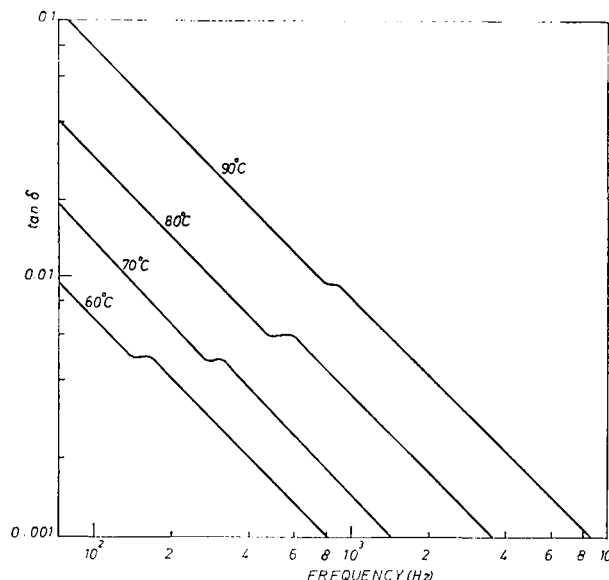


FIG. 3.

is free. The loss peak frequencies will then be primarily determined by bound vacancy jumps along $\langle 100 \rangle$. Activation energies for bound and free vacancies are known to be quite close (Barr and Lidiard 1970). If we interpret the region II of the conductivity as due to extrinsic cation vacancies which are released by dissociation of the impurity-vacancy dipoles, a binding energy of 0.55 eV is indicated for the interstitial-vacancy complex. Considering the intrinsic conduction to be only due to cation vacancies leads to a Schottky defect formation energy of 1.23 eV which may be compared with the calculated value (1.39 eV) (Table I).

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DISCUSSION

M. J. NORGETT. — Murti and Murthy have made comparison of the so called force balance and energy minimisation methods used in defect calculations in this field. We have compared the methods in several systems and found only small differences. In any case, this effect can only be a consequence of the small

relaxed region around the defect used in these calculations.

A more serious problem in this work arises from the use of the point polarisable ion model. It is well known now that this gives defect energies that are too low, especially for very polarisable materials

like the ammonium halides (for a comparative study of CsCl using point polarisable ion and shell models see paper by Muller and Norgett in these proceedings). I think this error must call into question, the interpretation of the ammonium halide results by a simple vacancy conduction mechanism.

A. L. LASKAR. — Degradation of material makes it difficult to explore the conductivity and diffusivity

in ammonium chloride. Recently we are measuring conductivity and self-diffusion of chlorine in this system. It appears that at about 170 °C the Arrhenius behavior of conductivity undergoes drastic change — with lower activation energy. Also we are doing the tracer diffusion of chlorine in ammonium halides. At lower temperature anion defects seem to be the principal charge carrier.