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IONIC TRANSPORT IN CADMIUM FLUORIDE

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Résumé. — Ces dernières années, les études de CdF_2 ont connu un grand essor en raison de sa faculté de se transformer d'un isolant à un semiconducteur. Cette conversion est permise par le désordre thermique du réseau, constitué de défauts de Frenkel dans le sous-réseau des anions. A l'encontre des études détaillées des propriétés optiques et diélectriques à basse température, les données à haute température sur le transport ionique intrinsèque et la structure du défaut dans ce cristal sont encore incomplètes et contradictoires. Dans cet article, des résultats expérimentaux récents sur la conductivité ionique et l'autodiffusion dans CdF_2 non converti sont réexaminés. Nous tentons de mettre des limites aux valeurs probables des paramètres du désordre et nous montrons que quelques aspects des résultats vont au-delà du domaine du transport ionique dans les solides accessibles par la théorie classique.

Abstract. — In recent years, CdF_2 has attracted considerable interest owing to its ability to be converted from an insulator to a semiconductor. This convertibility is rendered possible by the thermal disorder of the lattice, consisting of Frenkel defects in the anion sublattice. Contrary to extended investigations of the low-temperature electrical and optical properties, data on high-temperature intrinsic ionic transport and defect structure in this crystal are still incomplete and controversial. In this paper, recent experimental results on ionic conductivity and self-diffusion in unconverted CdF_2 are revised. We try to set limits to the probable values of the disorder parameters and show that some features of the results go beyond the reach of the classical theory of ionic transport in solids.

Current interest in CdF_2 dates from the discovery [1] that this ionic crystal can be converted to a semiconductor, in contrast to its otherwise striking similarity to CaF_2 , including Frenkel disorder in the anion sublattice. The conversion is achieved by doping the material with certain trivalent cations (Mf^{3+}) and annealing in Cd vapour at $\approx 500^\circ\text{C}$. This process follows the reaction equation

expressing the replacement of interstitial fluorine ions F'_0 by electrons via diffusional migrations to and from the surface [2]. Reaction (1) is enabled energetically by the annihilation of a lattice defect per electron incorporated. A similar argument excludes the creation of anion vacancies $\square'_a$ by a conversion reaction analogous to (1) [3]. This explains the necessity of Mf^{3+} additions ($\rightarrow \text{Mf}'_c$) in convertible CdF_2 crystals in order to provide a sufficient concentration of charge-compensating F'_0 . The other important function of these additions is to act as shallow traps for the electrons, effecting the semiconducting properties [4] of the converted material.

From the foregoing, it is evident that accurate knowledge of the parameters for point defect forma-

tion and migration would considerably improve the understanding and control of the conversion process. Unfortunately above 300°C the high aggressivity of CdF_2 and of its dissociation products causes increasing contamination because Cd vapour and F_2 react with most vessel and electrode materials. This entails increasing danger of falsified and/or controversial results. In fact values of the defect formation enthalpy between 4.5 and 0.4 eV have been derived from experimental results.

Figure 1 shows some typical conductivity data by Cyris [5], preferentially using evaporated silver electrodes. The curves pertaining to the same Sm^{3+} doped crystal after annealing either in Cl_2 or in Cd vapour exhibit the enormous influence of the conversion on the conductivity, enhancing it by more than 10^{10} at 20°C . Therefore special precautions are needed to ensure pure ionic conductivity in CdF_2 doped with Mf^{3+} . An anneal in Cl_2 gas (500°C , 1 h) prior to measurement has proven sufficient. Without such precaution, it is easy to obtain various intermediate curves, corresponding to a partly converted state. Results of this kind [7] include remarkable effects of storage and are probably due to electronic conduction.

The Na^+ and Se^{2-} doped crystals (Fig. 1) conduct much better than the Sm^{3+} and In^{3+} doped ones. This indicates incorporation of Na^+ on Cd^{2+} sites (Na'_c), of Se^{2-} on F^- sites (Se''_a) and the mobility of the charge-compensating F'_0 surpassing by far that of F'_0 .

(¹) Subscripts a, c, 0 indicate the incorporation on anion, cation or interstitial site, superscripts $\cdot, \cdot'$ give the excess charge, and g means gas phase, f surface.

FIG. 1. — Conductivity of CdF_2 crystals with various additions [5]. Nominal (as-weighed) concentrations. The Mf^{3+} doped crystals have been annealed in Cl_2 or Cd vapour.

The excellent linearity of these curves over 10 to 14 powers of 10 is typical for the association region. From this slope and that of the short extrinsic dissociated region, values of the enthalpies of association and vacancy motion were derived by computer adaptation (Table I). These values compare moderately

well with those obtained by other authors using similar conductivity results [6], [7] and the temperature dependence of the F^- self diffusion coefficient [8], which increases with rising Na^+ addition as it should do in the extrinsic region.

The next columns in table I give the experimental slopes of the conductivity curves in the association regions, inherent also in ITC measurements [9]. The bracketed value occurs only at unusually low temperatures (-80°C) and is perhaps disfigured by electronic contributions. As long as there is doubt about association of Mf^{3+} with F_0' , the last column represents an upper limit for H_{m0} , the enthalpy of F_0' motion, taking account of the bulge [10] to be expected near this region because of « salting-out » of the more mobile vacancies by Mf^{3+} .

This moderate conformity of results by different authors is entirely lost if we turn to the intrinsic conductivity region, which reaches to the melting point (mp) 1078°C and is governed by the formation enthalpy (H) and entropy (S) of the anion Frenkel defects. Within this region no reliable bulk transport measurements exist and perhaps never will be possible. At the lower boundary $\approx 400^\circ\text{C}$, those by Tan and Kramp [6] are the most credible ones in virtue of special experimental precautions, including anneals in F_2 prior to measurements.

The remarkable features of these results (Fig. 2) are first, knees on the $\lg T(1/T)$ curves of the Y^{3+} doped, undoped and weakly Na^+ doped crystals at $\approx 250^\circ\text{C}$, followed by very steep rises (2.69 eV) from 300°C upward, and second, intersections of these curves with those of the more strongly Na^+ doped samples. This rise, comparable only to a likewise extreme one found on SrCl_2 [14], is interpreted by the authors as intrinsic, yielding the enormous formation enthalpy 4.5 eV ($2.69 = 0.44 + 4.5/2$), which surmounts appreciably the maximum value 2.8 eV (CaF_2) ascribed formerly

TABLE I

Enthalpies of motion and association in eV

Authors	Addition	Enthalpy of		$H_{m0} + \frac{1}{2} H_{a0}$	Addition	$H_{m0} + \frac{1}{2} H_{a0}$
		motion H_{m0} (□ _a ')	association H_{a0} (□ _a ' Mf'_0 , □ _a ' Xf'_0)			
Cyril [5]	Na^+	0.43	0.42	0.63	In^{3+}	1.5
	Se^{2-}	0.38	0.60	0.68		
Tan, Kramp [6]	Na^+	0.52		0.69	In^{3+}	1.1 ... 1.5 (0.89)
		0.44		0.59 ... 0.27		
Kessler, Caffyn [7]	Na^+	0.51	0.64	0.88	In^{3+}	
Süptitz, Brink, Becker [8]	Ag^+ (?)	0.39				
Kunze, Müller [9]	Li^+			0.59	In^{3+}	1.02
	Na^+			0.66	La^{3+}	1.02
	Ag^+			0.68	Gd^{3+}	1.11

FIG. 2. — Conductivity of CdF_2 with Na^+ and Y^{3+} additions (analyzed concentrations) after Tan and Kramp [6], compared to results by Cyris [5] (210 ppm Sm^{3+}) and Kessler and Caffyn [7] undoped, A fresh sample, thickness 0.133 cm, B used sample, 0.19 cm).

to alkaline and alkaline-earth halides. Linear extrapolation of this rise to the mp would yield an « ionic superconductivity » of $\approx 10^{12} \Omega^{-1} \cdot \text{cm}^{-1}$ at that temperature. Therefore the steep rise cannot be part of the intrinsic region, the more so because this would preclude the intersections, instead of section-free smooth junctions of the Na^+ curves into the common intrinsic branch to be expected [11]. Such crossing can only result from an interchange of the roles of the two defect species as faster and slower carriers below the intrinsic region. In order to arrive at the mp with a sane conductivity value, several (at least 2) interchanges of this kind should occur, implying heavily temperature-dependent enthalpies and entropies of motion, i. e. several competing jump mechanisms. Such rather ad hoc assumptions would be of little use for computer analysis. A hypothetical solid-phase transformation of CdF_2 below its mp would be an expe-

dient, of course, but no such transformation is known for any compound crystallizing in the high-symmetrical fluorite lattice [15]. Therefore it seems inevitable to conclude that the steep rise (2.69 eV), if not due to contamination or surface effects, is an electronic perturbation effect of unknown origin, perhaps somewhat reminding of ZnO .

In this connection it is comforting that the steep rise is not seen on Kessler and Caffyn's conductivity curves of undoped crystals in the range 200 to 550 °C which, though not free from electrode effects, exhibit knees at ≈ 400 °C followed by a high-temperature slope 1.9 eV (Fig. 2). This would extrapolate to $\approx 10^4 \Omega^{-1} \cdot \text{cm}^{-1}$ at the mp, still a quasi-metallic value, whereas the conductivities of other simple halide crystals hardly exceed $1 \Omega^{-1} \cdot \text{cm}^{-1}$ at the mp.

Another possibility of calculating the disorder parameters is offered by the conductivity isotherms of Tan and Kramp [6], exhibiting both branches of the Koch-Wagner hyperbola at 200, 175 and 150 °C and therefore enabling a complete analysis including defect association [13]. The first values of the (molar) defect concentration x_0 of the pure crystal, as obtained by separate analysis of the Na^+ branches [6], have been criticized [11] because of the resulting low H (0.396 eV) involving a large negative S . For a crude estimate, we assume in figure 2 at 175 °C the conductivity of a pure crystal to be 1/10 of that of the undoped sample ⁽²⁾, i. e. $\sigma_0(175^\circ\text{C}) = 1.2 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$. This corresponds to $x_0(175^\circ\text{C}) = 1.9 \times 10^{-7}$, 1/10 of the published [6] value. Then (Fig. 3) the assumption $S = 5k$, consistent with the defect formation entropy of comparable crystals, yields $H = 1.41$ eV. Hence $x_0(\text{mp})$ would amount to 0.04 which is more than the maximum value 0.01 found on other simple ionic crystals like CaF_2 [12]. Reducing $x_0(\text{mp})$ to this value 0.01 entails other dilemmas (Fig. 3): Either S almost vanishes, or $x_0(175^\circ\text{C})$, as estimated from the isotherms, is very wrong and should be replaced by 3×10^{-9} . This value, however, would lead to unreasonably large vacancy mobilities $u_{\square}$ at 175 and 1078 °C. Therefore, if a compromising value of H exists within the entire temperature range of solid CdF_2 , it should be close to 1.41 eV.

The fluorine self-diffusion experiments [8] traced the intrinsic region only from 450 °C upward and led to the estimate $H = 2.1$ eV and $S = 4.61k$ ⁽³⁾ (Fig. 3). This gives a reasonable $x_0(\text{mp})$. However the resulting $x_0(175^\circ\text{C})$ seems to be much too low to account for the conductivity data, requiring

$$u_{\square}(175^\circ\text{C}) > 1 \text{ cm}^2/\text{Vs}.$$

Finally, it is enlightening to compare the ionic conduction of CdF_2 to that of CaF_2 (Fig. 4) [12]. This

⁽²⁾ Taking account of a probable unwanted impurity like Na^+ in the latter.

⁽³⁾ Introducing in eq. (6) of reference [8] the correct pre-exponential factor 2 instead of 1.

FIG. 3. — Extrapolation of the defect concentration x_0 to the melting point. k Boltzmann constant.

material allows a much closer approach to its mp 1418 °C. The disorder parameters come out to be somewhat smaller than previous values: $H = 2.43$ eV, $S = 7.95$ k , $H_{m\Box} = 0.51$ eV, $H_{m0} = 0.92$ eV [12]. The two charge carriers $\Box_a^+$ and F_0^- interchange their faster/slower roles at 670 °C; a similar behaviour can be anticipated for CdF_2 in view of the strong temperature dependence of the mobility ratio [6]. Figure 4 exhibits once more the anomaly of the steep conductivity rise of CdF_2 above 250 °C which hardly can be ascribed to ionic conduction in the bulk. Furthermore, assuming comparable behaviour of the

FIG. 4. — Comparison between the conductivities of CdF_2 [5], [6] and CaF_2 [12].

mobilities, it is evident that for CdF_2 H and S must be considerably smaller than for CaF_2 .

Throughout this paper, estimates of disorder parameter values from various experimental sources were subjected to the criterion that the resulting defect concentrations and mobilities up to the melting point must remain within certain limits compatible with the lattice defect model. Likewise the enthalpies and entropies of defect formation, migration and association should not differ too much from the values found on other comparable ionic crystals and especially should not become negative. *Faute de mieux*, this procedure may prove to be helpful in other cases of unknown or inaccessible high-temperature transport data as well. At any rate, new and precautionary experimental approaches to the high-temperature transport phenomena in CdF_2 are urgently needed.

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DISCUSSION

A. KESSLER. — I would like to remind, that the data of Caffyn and me used in figure 2 are the reciprocal values of the resistance of the samples per unit surface and thickness. That is because especially in the range we believe to be due to intrinsic conductivity there is a contribution of the « electrode resistance » to the measured resistance (see curves *A* and *B*). An extrapolation of these data is therefore not very meaningful in my opinion.

As far as the steep rise found by Tan and Kramp is concerned we also observed such a steep increase at about 500 °C. Moreover the current began to rise spontaneously at fixed voltage and temperature. If the voltage was immediately removed the sample recovered its original resistance at lower temperature. If the voltage was sustained for some time the original values of the resistance were « restored » and after removing the crystal surface, appeared colored after the said procedure.

This shows that (1) some chemical reaction or electron injection takes place at high temperatures and (2) there are differences in the material used by

the different authors due to sample preparation which are in my opinion still not understood or recognised.

J. TELTOW. — I agree with you that all these conductivity data are of preliminary character and should be checked and supplemented under definite experimental conditions.

J. Z. DAMM. — The anomalies observed in the conductivity curves of the doped CdF_2 crystals resemble the effects related with electron injection (electrolytic colouration) e. g. into Sr^{2+} -doped KCl performed *at flat electrodes*. This is consistent with the observations of Kessler mentioned earlier. The electron injection is sensitive to the heating rate and the dopant concentration. Especially, the effect of the former parameter should be carefully checked in the case of the anomalies cited by Dr. Teltow.

H. TELTOW. — Such injection would have caused thermal hysteresis effects. However, only reproducible conductivity data free from hysteresis have been plotted in figures 1 and 2 below 350 °C.