Anion disordering and specific heat of $Cd_{1-x}Pb_xF_2$ superionic crystals

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Abstract. The results of a study of the thermodynamic, electrical and x-ray scattering properties of $Cd_{1-x}Pb_xF_2$ crystals are presented. The parameters of the transition to the super-ionic state have been determined. A correlation has been found between ionic conductivity and the super-ionic-state transition temperature in $Cd_{1-x}Pb_xF_2$ crystals.

1. Introduction

Of all the super-ionic fluorite crystals, PbF_2 crystals have the lowest transition temperature to the super-ionic state ($T_c \simeq 700$ K) and the highest degree of fluorine sublattice disorder [1, 2]. Moreover, PbF_2 crystals are characterised by the lowest cation–anion interaction coefficient [3]. This interaction determines the dynamics and the electric properties of the crystals. The above-mentioned features of PbF_2 are probably connected with the valence electron configuration in the Pb ions which is different from those of other cations in fluorite-structure crystals. Elements belonging to group II in the periodic table, i.e. Ca, Sr, Ba and Cd, have an ns^2 valence electron configuration whereas, for Pb, the corresponding configuration is $6s^26p^2$. This results in a different band structure for PbF_2 compared with other fluorites. For the typical fluorites (CaF_2, SrF_2, BaF_2 and CdF_2), the valence band is formed by 2p electron states of F^- ions. The contribution from localised cation states—Ca^{2+}, Sr^{2+}, Ba^{2+} and Cd^{2+}—as seen from Madelung energy calculations, is negligible [4]. The opposite situation occurs in PbF_2 crystals. On the basis of the calculated Madelung energy, it can be shown that the F^- 2p electron level lies below the Pb^{2+} 6s level by about 1.5 eV. For this reason, Pb^{2+} 6s electron states will contribute significantly to valence band formation in PbF_2 crystals. The complex character of the valence band in PbF_2 crystals has been confirmed by photo-emission measurements [5], which have yielded results in good agreement with the band structure calculated in [4].

The remaining fluorites have band structures typical of ionic crystals; the valence bands consist of F^- 2p electron states, whereas the conduction bands are formed by s-type cation states.

Photo-emission measurements of CdF_2 indicate that the band structures of these crystals are typical of fluorite-structure crystals, with the binding energies of F^- 2p and

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Cd^{2+} 4d electron states comparable with the values calculated solely on the basis of the Madelung energy [6]. CdF_2 and PbF_2 crystals form solid solutions over the full compositional range [7], and studies of $Cd_{1-x}Pb_xF_2$ mixed crystals may thus yield interesting information on the crystal electronic and super-ionic properties, especially when the crystal passes from a super-ionic crystal (PbF_2) to an ionic crystal (CdF_2). The complex character of the PbF_2 valence band is manifested in the anomalous properties of $Cd_{1-x}Pb_xF_2$ mixed crystals in the fundamental absorption region [8]. Non-monotonic crystal compositional dependence of the absorption edge is one of the most characteristic features. The mixed-crystal lattice dynamics and ionic transport properties exhibit similar anomalies. For $Cd_{1-x}Pb_xF_2$ crystals with $0.4 \lesssim x \lesssim 1$, only weak changes are observed in the cation–anion interaction coefficients and the activation energy of the conductivity [9]. Studies of $Cd_{1-x}Pb_xF_2$ mixed crystals may help us to determine the role played by the cation sublattice in anionic defect formation processes responsible for the super-ionic properties of crystals. The degree of anion sublattice disordering determines the parameters of the transition to the super-ionic state. A typical method of observing the transition is based on specific heat measurements. The temperature corresponding to a specific heat anomaly is taken to be the transition temperature [2, 10]. The presence of such specific heat anomalies is ascribed to collective interactions of anionic Frenkel defects [10].

High defect concentrations in PbF_2 crystals and strong anharmonic lattice oscillation effects lead to anomalies both in the Raman spectra [11, 12] and in the temperature dependences of the lattice constant [13, 14]. The strong disordering in the anion sublattice of PbF_2 crystals is also manifested in the polarisation effects [15, 16]. On the basis of the latest studies of ionic transport in $Cd_{1-x}Pb_xF_2$ crystals [9], it may be concluded that these crystals possess a higher ionic conductivity and a lower activation energy of conductivity that does PbF_2. For the mixed crystals, measurements of the temperature of the transition to the super-ionic state may thus yield data on anionic defect formation processes.

In the present work, the results of a study on the thermodynamic and x-ray scattering properties of $Cd_{1-x}Pb_xF_2$ crystals are presented. The aim of this work is to determine the influence of the $Cd_{1-x}Pb_xF_2$ crystal cation sublattice disorder on the crystal super-ionic properties, and to investigate the relation between ionic conductivity and the parameters of the transition into the super-ionic state.

2. Samples and experimental details

$Cd_{1-x}Pb_xF_2$ crystals were obtained using the zone-melting method. The growth process was carried out in spectrally pure graphite crucibles in an Ar atmosphere [7].

The specific heat measurements (i.e. the differential thermal analysis (DTA)) were performed with a Seteram DSK-2 calorimeter. Samples of $Cd_{1-x}Pb_xF_2$ crystals placed in sealed quartz ampoules were heated at a rate of 5 K min^{-1} in the temperature range 300–800 K.

The resulting data on the specific heat were analysed using a model which took into account both the $Cd_{1-x}Pb_xF_2$ crystal anion point non-equivalence, connected with the different fluorine ion environments, and the contribution to the crystal free energy arising from changes in the ion oscillation frequency [17].

Temperature measurements of the lattice constant were carried out with a DRON-3 x-ray diffractometer, in the temperature range 300–800 K.
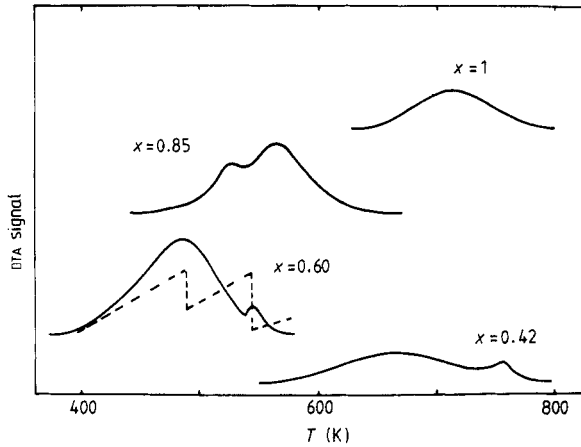
Figure 1. The temperature dependence of the specific heat for $Cd_{1-x}Pb_xF_2$ mixed crystals: – – –, calculation result.

3. Results and discussion

Figure 1 shows the temperature dependences of the specific heat for $Cd_{1-x}Pb_xF_2$ mixed crystals. As the value of x was increased in the range $0.6 < x < 1$, a decrease was observed in the specific heat peak temperature, and thus a decrease in the temperature of the transition to the super-ionic state. For $0 < x < 0.6$, a rise in the temperature of transition to the super-ionic state was seen. At the same time, for $Cd_{1-x}Pb_xF_2$, some additional anomalies were observed. The observed anomalies are probably due to a change in the local anion sublattice point symmetry. These anomalies may be described within a phenomenological model which takes into account mutual interactions of defects and the differences in their formation energies [17]. For $Cd_{1-x}Pb_xF_2$ mixed crystals, there are five types of fluorine ion neighbourhood, i.e. five different ways of arranging Cd and Pb ions. We expect these different anion neighbourhoods to correspond to different Frenkel defect formation energies. The expression for the free energy of $Cd_{1-x}Pb_xF_2$ thus has the form

$$f = \frac{F}{N_s} = \sum_{i=0}^{4} E_i C_i - \frac{1}{2} \sum_{i,j=0}^{4} \alpha_i \alpha_j C_i C_j (1 + \delta_{ij}) + kT \left((1 - C) \ln(1 - C) + C \ln C \right.$$

$$\left. + \sum_{i=0}^{4} m_i C_i \ln(m_i - C_i) + \sum_{i=0}^{4} C_i \ln C_i - \sum_{i=0}^{4} m_i \ln m_i + 3C \ln \Gamma \right) \quad (1)$$

where N_s denotes the number of the anion sublattice points $i = 0, 1, \ldots, 4$, corresponding to the five distinct neighbourhoods of a fluorine ion, containing respectively 0, 1, 2, 3 and 4 Cd atoms, E_i and C_i denote the formation energy and concentration of anion Frenkel defects $(C = \Sigma_{i=0}^4 C_i)$, respectively, α_{ij} is the defect interaction parameter, and $m_i N_s$ denotes the number of interstitial positions in the crystal lattice which can be occupied by fluorine ions. For the fluorite structure, the following condition is satisfied: $\Sigma_{i=0}^4 m_i = \frac{1}{2}$. Γ is the average anion oscillation frequency change due to crystal defects. Minimising the free energy $(\partial f / \partial C = 0)$, we obtain the following:

$$\ln\left(\frac{C}{1-C}\right) + \sum_{i=0}^{4} \ln\left(\frac{C_i}{m_i - C_i}\right) = -3\ln\Gamma - \frac{1}{kT}\left(-\sum_{i=0}^{4} E_i + \sum_{i=0}^{4} \sum_{j\geqslant 0}^{4} d_{ij}(C_i + C_j) \right) \quad (2)$$

and the specific heat will thus be expressed as

$$C_p = \frac{1}{k^2 T^2} \left(\sum_{i=0}^{4} E_i - \sum_{i=0}^{4} \sum_{j=0}^{4} \alpha_{ij} (C_i + C_j) \right)^2$$

$$\times \left(\frac{1}{C(1-C)} + \sum_{i=0}^{4} \frac{m_i}{C_i(m_i - C_i)} - \frac{2}{kT} \sum_{i,j=0}^{4} \alpha_{ij} \right)^{-1}. \tag{3}$$

Equations (2) and (3) may be solved by numerical methods.

In the model discussed, the creation energy of Frenkel defects is determined, to a first approximation, by the interaction between the fluorine ion with its nearest neighbours. The energy changes connected with defect incorporation do not play an essential role. This interpretation is typical of energy parameter calculations for doped ionic crystals. Since there were two specific heat maxima for $Cd_{1-x}Pb_xF_2$ mixed crystals, to a first approximation, we took account of two effective anion near-neighbour configurations with different energies E_i. In figure 1 the results of calculations for the $Cd_{0.4}Pb_{0.6}F_2$ crystal are shown by a broken line. In the calculations, the following parameter values were assumed: $E_1 = 0.94$ eV, $E_2 = 0.6$ eV, $m_1 = 0.3, m_2 = 0.2, \alpha_{11} = 1.88$ eV, $\alpha_{12} = 1.41$ eV, $\alpha_{22} = 0.94$ eV, $\Gamma = 0.21$. The energy E_1 corresponds to the anion Frenkel defect formation energy in a PbF_2 crystal [18], whereas E_2 was derived from experimental data on the ionic conductivity of a $Cd_{1-x}Pb_xF_2$ crystal [9]. Values of $\alpha_{ij} \simeq E_i$ are characteristic of those for a super-ionic conductor [19]. The calculations performed using the above phenomenological model have allowed us to describe quali-
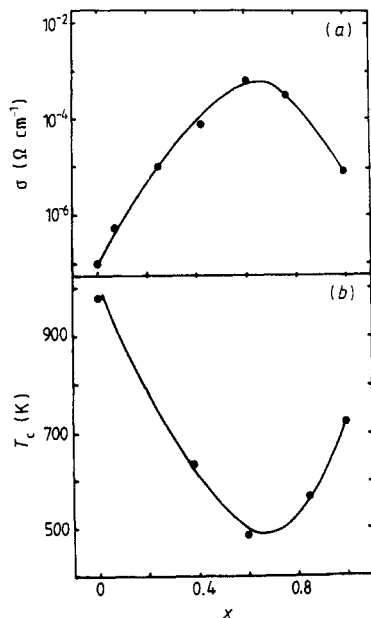

Figure 2. The x dependences of (a) the ionic conductivity σ (at 400 K) and (b) the super-ionic state transition temperature T_c for $Cd_{1-x}Pb_xF_2$ crystals.

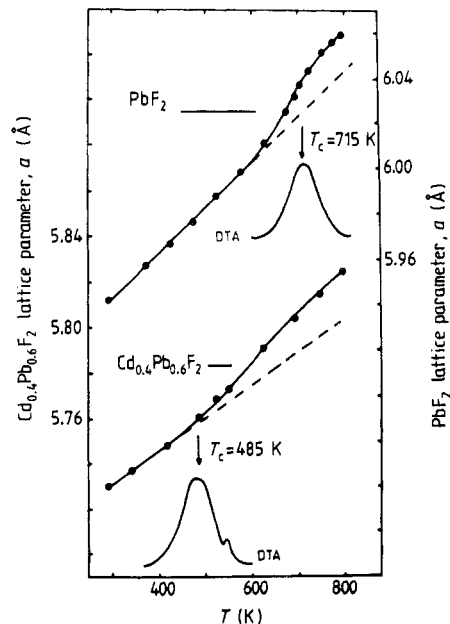**Figure 3.** The temperature dependence of the lattice constant and the specific heat for PbF_2 and $Cd_{0.4}Pb_{0.6}F_2$ crystals.

tatively the temperature dependence of the specific heat for Cd$_{1-x}$Pb$_x$F$_2$ crystals around the temperature of the transition to the super-ionic state. The temperatures at which the specific heat anomalies were predicted to occur are in agreement with the experimental data (figure 1).

The specific heat anomalies observed by us, arising from the transition of a mixed crystal to the super-ionic state, may be qualitatively interpreted in terms of cation sublattice-rearrangement-induced anion point non-equivalence. These processes determine the configurational entropy of a crystal. Taking into account the anion oscillation frequency change in a defective crystal leads not only to a change in transition temperature T_c but also to some other specific heat anomalies. It should be pointed out that the specific heat anomalies were seen only for Cd$_{1-x}$Pb$_x$F$_2$ mixed crystals. Previously, Ba$_{1-x}$La$_x$F$_{2+x}$ [20] and Pb$_x$U$_{1-x}$F$_{2+x}$ solid solutions have been studied [21]. It had been found that T_c was hardly dependent on crystal composition, and significant broadening of a temperature dependence of the specific heat had been observed. It was shown that these anomalies could be described by taking into account only the effects of the change in the configurational entropy.

For the crystals investigated in this work (i.e. Cd$_{1-x}$Pb$_x$F$_2$), the contribution to the free energy due to the change in ion oscillation frequency was found to be essential. As the Pb content in the Cd$_{1-x}$Pb$_x$F$_2$ crystals was changed, a non-linear compositional dependence of the transition temperature T_c was observed (figure 2) which for $x = 0.6$ attained a minimum at $T_c = 485$ K. The disordering effects in Cd$_{1-x}$Pb$_x$F$_2$ crystals manifest themselves both in a compositional dependence of ionic conductivity and in the half-width of the Raman line [22]. The compositional dependence of the ionic conductivity attains a maximum for $x = 0.6$ (cf figure 2), which coincides with the minimum transition temperature.

The crystal conductivity is determined by the concentration and mobility of electric carriers. The correlation observed for Cd$_{1-x}$Pb$_x$F$_2$ between the conductivity maximum and the minimum transition temperature indicates that the dominant contribution to the compositional dependence of the conductivity is due to the ion concentration change caused by the change in the crystal composition, and this also determines the temperature of the transition into the super-ionic state. The effects of disorder in the fluorine sublattice are seen in temperature measurements of the lattice constant. For PbF$_2$ crystals, there is a deviation from linear dependence at temperatures above 600 K (figure 3) [13, 14]. It should be pointed out that, at these temperatures, specific heat anomalies are also observed [4, 13]. Both these effects are connected with the thermal generation of Frenkel defects.

For Cd$_{1-x}$Pb$_x$F$_2$ mixed crystals, we expect to observe that the anomalies in the dependence of the lattice constant shift to lower temperatures owing to a decrease in the super-ionic phase transition temperature. In figure 3 the temperature dependences of the PbF$_2$ and Cd$_{0.4}$Pb$_{0.6}$F$_2$ lattice constants are shown. For PbF$_2$, an anomalous increase in the lattice constant is observed at $T > 620$ K whereas, for Cd$_{0.4}$Pb$_{0.6}$F$_2$, this occurs at $T > 480$ K. For the Cd$_{1-x}$Pb$_x$F$_2$ crystals investigated, a correlation was found between the specific heat and lattice constant anomalies (figure 3). These crystals are characterised by better super-ionic properties than PbF$_2$. This is manifested in the rise in ionic conductivity, the drop in the activation energy of conductivity and a decrease in the super-ionic state transition temperature (figure 2). For Cd$_{0.4}$Pb$_{0.6}$F$_2$ the super-ionic state transition temperature T_c is lowest and equals 485 K. The above results on the specific heat, ionic conductivity and lattice constants for Cd$_{1-x}$Pb$_x$F$_2$ crystals indicate that the cation sublattice plays an important role in the anion disordering processes.

4. Conclusions

The results reported of investigations of $Cd_{1-x}Pb_xF_2$ crystals show that the disordering of the cation sublattice, which takes place as the crystal changes from CdF_2 to PbF_2, enhances its super-ionic properties. This is manifested mainly in the rise in crystal ionic conductivity and in a significant decrease in the super-ionic phase transition temperature (figure 2). The specific heat anomalies observed may be uniquely described by taking into account both anion sublattice point non-equivalence and anion oscillation frequency change in the mixed crystals. Such an approach renders it possible to explain not only a broadening of the temperature range for the transition to the super-ionic state but also additional maxima in the specific heat (figure 1). The anomalies accompanying the anion sublattice disorder in $Cd_{1-x}Pb_xF_2$ crystals indicate the complex nature of the cation sublattice rearrangement and are found to be due to specific Pb ion valence electron configurations.

Acknowledgments

References

[1] Salamon M B (ed.) 1979 *Physics of Superionic Conductors* (Berlin: Springer)
[2] Hayes W 1982 *Light Scattering in Solids* ed. M Cardona and G Guntherodt (Berlin: Springer)
[3] Denham P, Field G R, Morse P L R and Wilkinson G R 1970 *Proc. R. Soc.* A **317** 55
[4] Velicky B and Mlasek T 1986 *Solid State Commun.* **58** 663
[5] Chab V, Kowalski B T and Orłowski B A 1985 *Solid State Commun.* **58** 667
[6] Orłowski B A and Langer J M 1979 *Phys. Status Solidi* b **91** K53
[7] Kosacki I and Dynowska E 1980 *J. Cryst. Growth* **50** 575
[8] Kosacki I and Langer J M 1986 *Phys. Rev.* B **33** 5972
[9] Kosacki I, Hibner K, Litvinchuk A P and Valakh M Ya 1986 *Solid State Commun.* **57** 729
[10] Riami D S and Sladek R T 1979 *Solid State Commun.* **31** 473
[11] Elliot R T, Hayes W, Klepman W G, Ruschworth A T and Ryan T F 1978 *Proc. R. Soc.* A **360** 317
[12] Kosacki I, Litvinchuk A P and Valakh M Ya 1985 *Solid State Commun.* **53** 373
[13] Koto K, Schulz H and Huggins R A 1980 *Solid State Ion.* **1** 355
[14] Kosacki I, Hibner K and Stefański T 1987 *Acta Phys. Pol.* A **71** 409
[15] Kosacki I 1988 *Solid State Ion.* at press
[16] Kosacki I and Zalibowski K 1988 *Acta Phys. Pol.* A **73** 403
[17] Windersich H and Tonston W V 1969 *J. Phys. Chem. Solids* **30** 1475
[18] Azimi A, Carr V M, Chadwick A V, Kirkwood F G and Saghafian R 1984 *J. Phys. Chem. Solids* **45** 23
[19] O'Reilly U B 1978 *Phys. Status Solidi* a **48** 489
[20] Andersen N H, Clausen K N, Kjems T K and Schoonman J 1986 *J. Phys. C: Solid State Phys.* **19** 2377
[21] Andersen N H, Clausen K N and Kjems T K 1983 *Solid State Ion.* **9–10** 543
[22] Ciepielewski P and Kosacki I 1982 *Solid State Commun.* **44** 417