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# The temperature-dependent structure of point-defect complexes in silver chloride crystals

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**Abstract.** Evidence of a temperature-induced, cyclable transition in the structure of point-defect complexes in AgCl crystals is reported. The effect is attributed to an entropy-driven change in the equilibrium structure of defect configurations, analogous to a phase transition in bulk solids. Such a transition is likely to occur in a system where the entropy term is a significant part of the defect Gibbs free energy, and where the energies of different defect configurations are very close. A crude thermodynamic analysis provides an estimate of the energy and entropy changes associated with the transition.

## 1. Introduction

The silver halides have proven to be a rich class of materials for the study of crystal lattice defects, partly because they have a simple structure with predominantly ionic bonding, and partly because they exhibit a complex array of defects and defect processes. Several of their defect characteristics, notably the large mobility of the interstitial silver ions and the ‘doping’ effect of multivalent cation impurities, are important for the manufacture of photographic films. In spite of several decades of intensive work, research on silver halides continues to yield steady improvements in the quality of photographic films and new insights into the fundamental properties of solids [1].

Since the 1960s the perturbed angular correlation (PAC) technique has been applied extensively and fruitfully to the study of metals [2] and semiconductors [3], including the study of crystal lattice defects. In spite of this success the technique has been applied to insulators only rarely. Except for a pioneering 1951 experiment, which failed to show an angular correlation for alkali and silver halides [4], the technique was not reported for the classic ionic materials until 1990 [5]. PAC is a powerful technique for studying the behaviour of defect complexes involving foreign atoms because it provides microscopic structural information about the region surrounding such atoms. Unlike most other techniques commonly used to study defect structure, PAC is useful over a broad range of temperatures—previous publications have documented investigations of the low-temperature structure [5] and higher-temperature dynamic behaviour [6] of indium–silver vacancy ( $\text{In-V}_{\text{Ag}}$ ) defects in silver chloride, and forthcoming papers will document similar complexes in silver bromide. A surprisingly complex picture of the equilibrium behaviour of point-defect complexes is emerging.

The present work focuses on reversible transitions occurring in the equilibrium structure of  $\text{In-V}_{\text{Ag}}$  complexes in AgCl in an intermediate temperature range. While similar behaviour is observed for similar complexes in AgBr, the situation there is somewhat more complex,

and will be discussed only briefly here. In this paper, data for In-V<sub>Ag</sub> complexes in AgCl will be analysed in terms of a simple thermodynamic model, allowing the extraction of the energies and entropies characterizing the transition.

## 2. Experimental details

PAC spectroscopy utilizes the radiation from implanted or diffused radioisotope probe atoms to measure the strength and symmetry of hyperfine interactions occurring at the site of the probe nucleus. In non-magnetic materials, whenever the probe atoms themselves are not magnetic, the magnetic dipole interaction vanishes; when gradients of the electric field exist, the electric quadrupole interaction is therefore the dominant hyperfine interaction. Because the electric quadrupole interaction is very local, vanishing as  $r^{-3}$  in ionic solids, this interaction provides a convenient way of studying asymmetries of the charge distribution in the immediate vicinity of the probe atoms, such as those arising from adjacent lattice defects. In favourable cases detailed information about the structure of defects can be obtained.

PAC monitors the nuclear spin precession caused by the electric quadrupole interaction between the probe nucleus and the electric field gradient (EFG) arising from asymmetries in the environment of the probe atom [7]. This is accomplished via measurement of the time-dependent perturbation of the angular distribution between the gamma ray  $\gamma_1$ , which populates the  $I = \frac{5}{2}$  isomeric state of  $^{111}\text{Cd}$ , the daughter of  $^{111}\text{In}$ , and  $\gamma_2$ , which depopulates that state. In practice a PAC experiment consists of the measurement of the number  $I_{ij}(\Theta, t)$  of coincidence counts between detectors  $i$  and  $j$  as a function of the angle  $\Theta$  between detectors, and the time  $t$  between the detection of  $\gamma_1$  and  $\gamma_2$ . It is customary to present PAC data in the form of a ratio  $R(t)$  of the  $I_{ij}(\Theta, t)$  spectra, in such a way that the time dependence of the angular correlation is directly displayed,

$$R(t) = A_{22}G^{\text{eff}}(\Theta, t). \quad (1)$$

Here  $G^{\text{eff}}(\Theta, t)$  is the time-dependent term arising from the quadrupole interaction, and is given, for static configurations, by

$$G^{\text{eff}}(\Theta, t) = f_0 + \sum_k f_k \left( S_{k0}^{\text{eff}} + \sum_{n=1}^3 S_{kn}^{\text{eff}} \cos(\omega_{kn}t) \exp[-(\sigma_{kn}t)^2/2] \right). \quad (2)$$

Here,  $f_k$  are the fractions of probe nuclei in a particular type of non-cubic site, designated by the index  $k$ . There is one term  $k$  for each type of defect complex that breaks cubic symmetry, and  $f_0$  is the fraction of  $^{111}\text{Cd}$  nuclei in a cubic environment, experiencing no electric field gradient. The  $S_{kn}^{\text{eff}}$  are related to the Clebsch-Gordan coefficients, and depend on the symmetry and the orientation of the EFG tensor measured at the nucleus, relative to the detectors. The frequencies  $\omega_{kn}$  depend on both the symmetry and the magnitude of the EFG tensor. The exponential factor in equation (2) accounts for the finite width of the EFG distribution. In practice the  $R(t)$  data are fitted to the relevant parameters from equation (2), using a least-squares fitting routine, yielding information on the fractions of probe nuclei in specific defect sites and the symmetries, orientations, and strengths of the EFGs associated with the defect configurations.

Roughly, equation (2) and the  $R(t)$  spectra displayed in the figures can be thought of as representing time-dependent projections of the correlated, precessing nuclear spins

onto some axis. If dynamic processes are present on a time scale such that the fluctuation frequency is comparable to the spin precession frequency, the correlation is destroyed to some extent over time, and equation (2) must be modified by the introduction of one or more decaying exponential terms [8]. The precise form of the modifications depends on the relative time scales involved, and for some fluctuation frequencies equation (2) fails and no analytical form for  $G^{\text{eff}}(\Theta, t)$  is obtainable. In cases favourable for the analysis of PAC data on fluctuating systems, information on the nature of the dynamic process causing the fluctuations can be obtained [6].

The measurements described below were made on pure crystals of AgCl grown by Mr Charles Childs of this laboratory using the Bridgmann method. Both single and polycrystalline samples were used. The single crystals were oriented, cut, polished and etched into pieces roughly  $2 \times 2 \times 10 \text{ mm}^3$ . Polycrystalline samples were prepared by cutting single crystals into many small pieces and then etching, thereby assuring random crystallite orientation to a good approximation while avoiding some of the difficulties associated with powder samples. Samples were doped with about  $10 \mu\text{Ci}(10^{11} \text{ nuclei})$  of  $^{111}\text{In}$  by drying an  $\text{InCl}_3\text{-HCl}$  solution on the surface of the material, enclosing the sample in a quartz capsule under a halogen atmosphere and annealing for 12 h or more at temperatures near the melting point. This procedure allows  $\text{InCl}_3$  to dissociate and the In to diffuse to a depth of the order of several tens of  $\mu\text{m}$  or more, resulting in an atomic fraction of the order of  $10^{-8}$ . Samples were cooled slowly to room temperature to minimize strain and placed into a closed-cycle liquid helium refrigeration system, where the slow cooling was continued until the desired temperature was reached. The samples remained in the quartz capsules during all measurements.

Measurements relevant to this work were all made between 12 K and 180 K. While EFGs are sampled by daughter  $^{111}\text{Cd}$  nuclei following the nuclear decay, at these temperatures the measured EFGs reflect the structure of defects originally near the mother  $^{111}\text{In}$  probe atoms, since ionic motion is frozen out in AgCl at these temperatures on a time scale comparable to the nuclear precession period and the lifetime of the intermediate state. It was argued in an earlier paper [5] that In occurs in AgCl predominantly in the trivalent state; hence in this range of temperatures PAC reveals information on the interaction of *trivalent In* with the silver halide lattice. This is corroborated by the results of the low-temperature structural studies of [5], which indicate that in general two vacancies are bound to the impurity, and by diffusion [9] and ionic thermocurrent [10] measurements that rule out the single ionized state. Because Ag vacancies form readily in silver halides and because electronic charge compensation is energetically unfavourable, the excess charge of the trivalent In ion is compensated by the creation of two Ag vacancies in the vicinity of the In impurity. The opposite charge of the In and the vacancies, relative to the Ag sublattice, cause the In and vacancies to bind, forming compound defects of various structure. Like molecules, these complexes can have quite diverse properties depending on their particular structure, notably with regard to hole- and electron-trapping behaviour [11]. This fact accounts for the use of multivalent cation impurities as dopants in practical photographic films [12].

### 3. Results

PAC data for pure single crystals of AgCl are shown in figure 1 for several temperatures between 100 K and 180 K. Figure 2 shows Fourier transforms for the same data. The remarkable feature of these data was the gradual transition occurring between 120 K and 180 K. This transition was reversible in the sense that as the temperature was raised and

then lowered, the new spectra were identical to spectra previously measured at the same temperatures. Measurements were made at temperatures as low as 12 K, but no change was observed in the PAC spectrum below 100 K. As the temperature was raised above 180 K no additional significant change in the spectrum was seen until the onset of diffusion-induced damping above 200 K. The spectra of figure 1 were taken with all four detectors aligned along  $\langle 110 \rangle$  axes. For temperatures below the 150 K transition, significant variations in these spectra were observed when the detector orientation was changed, as discussed in [5]. Above this transition the  $R(t)$  spectra did not depend significantly on the detector orientation.

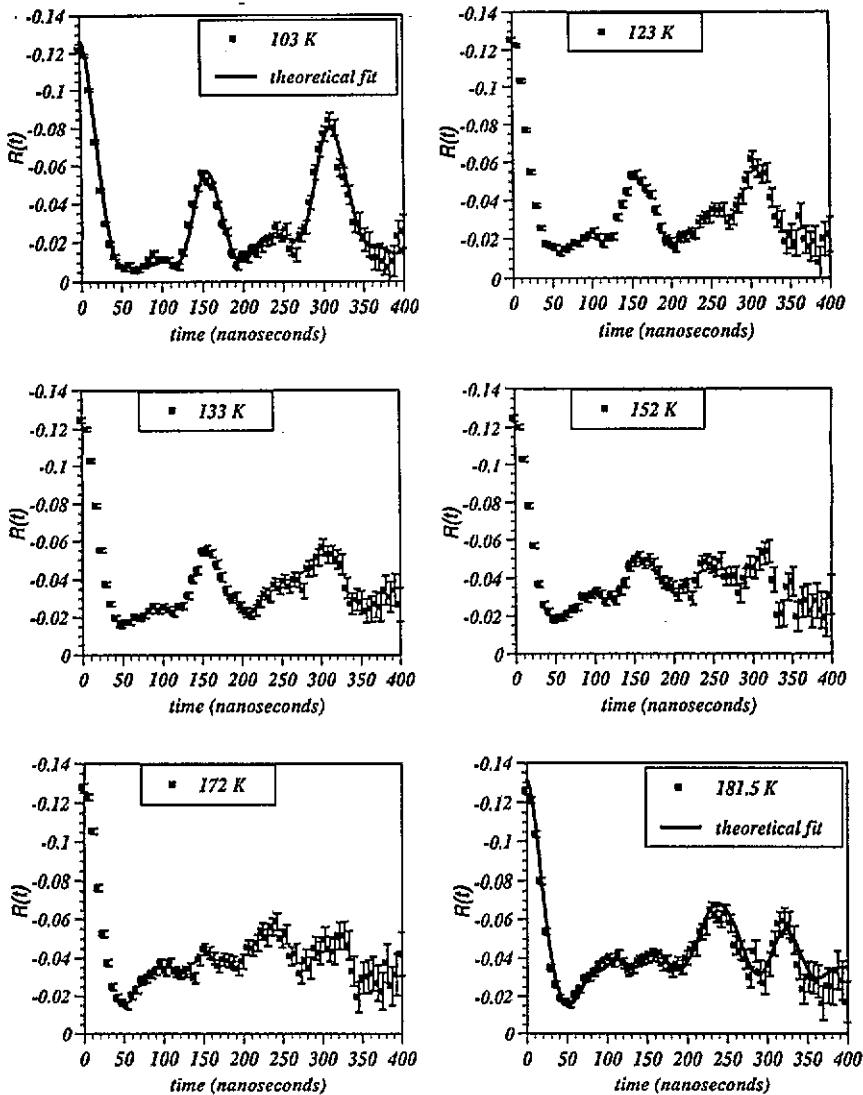


Figure 1.  $R(t)$  data for the  $\text{AgCl}:\text{In}$  system at several temperatures between 103 K and 181 K (see equations (1) and (2)). The data show a reversible transition centred near 150 K. Detectors subtend angles of  $90^\circ$  and  $180^\circ$ , and are aligned along  $\langle 110 \rangle$  axes. Fits to the theoretical equation (2) using the parameters listed in table 1 are shown at 103 K and 181.5 K. The four-fraction model does not provide reasonable fits at intermediate temperatures.

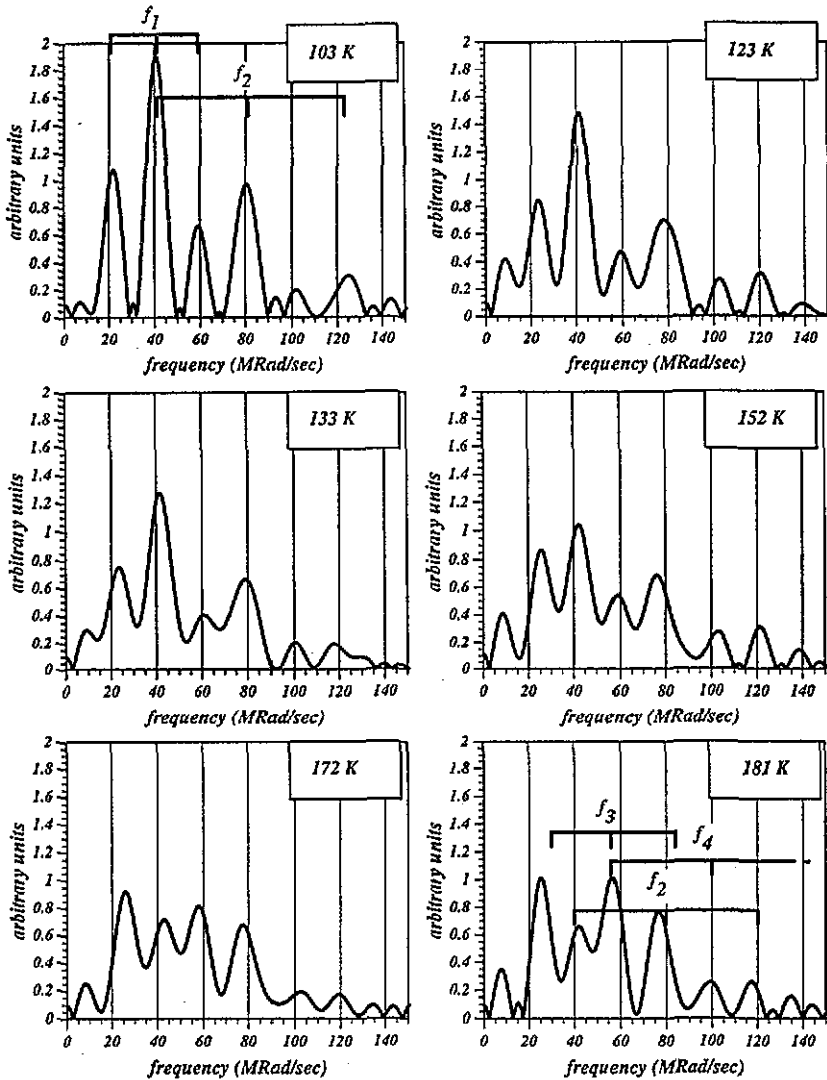


Figure 2. Fourier transforms for the data shown in figure 1, for the AgCl:In system.

Table 1. Fitting parameters for AgCl:In PAC spectra measured at 103 K and 181 K, as determined by a least-squares theoretical fit to the data using equation (2). In each box the 103 K values are listed first. Note that in warming from 103 K to 181 K, the fraction  $f_1$  has vanished completely,  $f_2$  has been considerably reduced, and both  $f_3$  and  $f_4$  have increased dramatically. All fractions have an uncertainty of  $\pm 5\%$ .

	$f_0$	$f_1$	$f_2$	$f_3$	$f_4$
Fraction (%)	22/20	31/0	34/13	9/51	4/16
$\nu_Q$ (MHz)	—	21.5/—	43/41	28/28	58/55
$\eta$	—	0/—	0	0	$\sim 0.4$

The first step in the quantitative analysis of static PAC quadrupole spectra is the

assignment of the various frequency components (seen as peaks in the Fourier transforms) to the frequency triplets associated with a unique defect configuration. Such an analysis was impossible in the vicinity of the 150 K transition, since the simple three-frequency model implicit in equation (2) breaks down in this region. The failure of equation (2) to accurately describe  $R(t)$  near the transition is probably due to fluctuations in the structure of the defects on a time scale comparable to the spin precession period, resulting in fluctuations in the magnitude and symmetry of the EFG tensor. Fluctuations such as these are likely to result from the hopping of vacancies between inequivalent lattice sites adjacent to the probe ion. No analytical form is available to describe the perturbation factor  $G^{\text{eff}}(\Theta, t)$  under these conditions [8]; hence, a detailed quantitative analysis would take us beyond the intended scope of the present work.

Even under the best conditions, at temperatures far from the transition, considerable uncertainty arises in the detailed analysis of the data because the spin precession frequencies are not large relative to the inverse of the total PAC time window. In particular, the 84 ns lifetime of the isomeric state of  $^{111}\text{Cd}$  allows useful data to be collected over about 400 ns. This limits the precision of frequency measurements to only 2.5 MHz, of the order of 10% of the measured quadrupole frequencies. The overlap of certain of the frequencies arising from different configurations aggravates this problem. These factors result in substantial measuring error; even in the best cases it is impossible to determine fractions to better than about 5%, and the frequencies carry an uncertainty of at least several MHz.

An analysis of AgCl data in the low- and high-temperature limits (at 103 K and 181 K, respectively) is given in table 1. At and below 103 K, four fractions appeared in the fit of the data to equation (2), three of which,  $f_2$ – $f_4$ , also appeared above the transition. Two of these fractions,  $f_3$  and  $f_4$ , were not clearly indicated by the Fourier transform at 103 K, and were perhaps too small to be considered significant. As mentioned above, this four-fraction model breaks down near the transition temperature, about 150 K. In [5] it was determined that  $f_2$  corresponds to a linear  $\text{In-V}_{\text{Ag}}$  complex with two vacancies, each occupying *next-nearest-neighbour Ag sites*, relative to the In probe (figure 3(a)). It was determined that  $f_1$  is either an In with a single bound vacancy at a next-nearest-neighbour position, or a right-angle next-nearest-neighbour divacancy configuration, as indicated in figure 3(b). Recent experiments have determined that  $f_1$  does, in fact, correspond to the In–divacancy defect shown in figure 3(b), since the relative fractions of the two dominant complexes were found not to depend on the concentration of free Ag vacancies, an indication that the complexes  $f_1$  are fully compensated. The fractions  $f_3$  and  $f_4$  were not identified. It is possible that these fractions represent substitutional In–vacancy complexes with one or both of the vacancies occupying nearest Ag neighbour sites. One factor, however, may contradict this interpretation: the independence from detector orientation of the spectra above the 150 K transition. PAC spectra arising from simple defect structures with low-order symmetry axes are expected to show a considerable dependence on the orientation of the gamma-ray detectors relative to the single-crystal axes. No such dependence was observed above the transition temperature. The absence of a dependence on the orientation might arise from a lowering of the symmetry of the defect complexes, as might be expected from a distortion or a strong relaxation of the constituents, perhaps an off-centre position of the In ion. In any case, information on the orientation of the defect-induced EFG tensor is obscured, and we are not able to present a definitive interpretation of the structure of the dominant complexes  $f_3$  and  $f_4$  above the transition.

The results obtained for similar complexes in AgBr were in many respects very similar to those discussed above for AgCl. There were, however, some intriguing differences. Measurements on AgBr are in progress, and will be discussed in detail in a later paper.

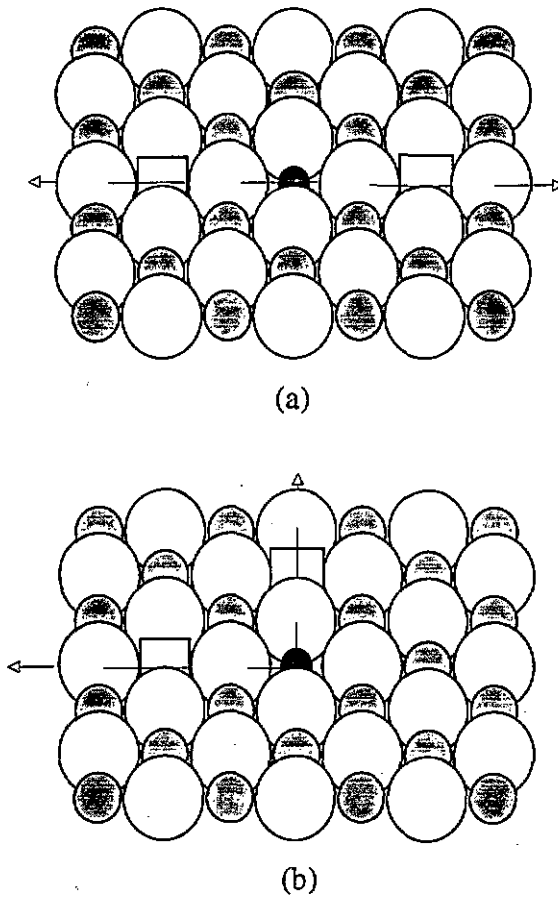


Figure 3. Low-temperature defect complexes for AgCl:In, as determined in [5]: (a) the defect giving rise to the fraction  $f_2$  appearing in AgCl at 103 K; (b) the defect giving rise to  $f_1$ . The small black central circles indicate In probe ions, the large unfilled circles represent Cl ions, and the small filled circles indicate Ag ions. The squares indicate Ag vacancies.

#### 4. Discussion

In this section we present three possible interpretations of the transitions presented in the data of figures 1 and 2. The first interpretation involves the ionization of the defect complex, an electron or hole being liberated from the 'dopant' defect as the temperature is raised. Such processes are, of course, common in doped covalent semiconductors. There are several arguments against such an interpretation in ionic materials such as the silver halides; notably, such a transition would require the existence of two electronic levels that are fairly close in energy, differing by only tens of meV, and this situation is rarely seen in ionic materials [13]. Such a process would not be likely to be reversible, since liberated carriers would become trapped elsewhere.

The second model is similar, but proposes that the trapped charge carrier is a hole arising from the decay of the isotope  $^{111}\text{In}$  to  $^{111}\text{Cd}$ . It is well known that many holes are created during the violent process of electron capture and the subsequent electronic relaxation [14]. In this model the observed transition results directly from the measurement, constituting an electronic 'after effect'. However, the hole mobility in silver halides is quite



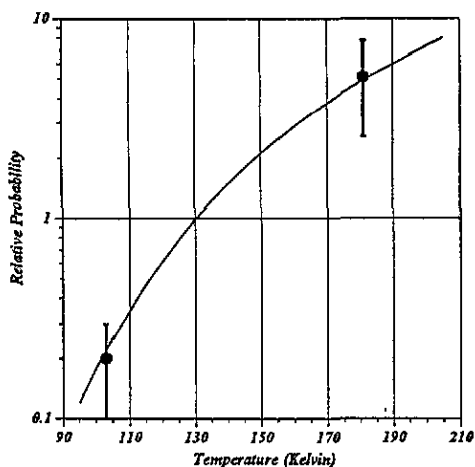


Figure 4. Plot of equation (3) for values of  $\Delta h$  and  $\Delta s$  appropriate to the observed transition in AgCl:In. The plot shows relative probabilities for two complexes different in enthalpy by  $\Delta h = 64$  meV and in entropy by  $\Delta s = 5.7k_B$ . The transition is centred at the temperature where the relative probability for the two complexes is equal to one.

large, and the valence-band energy lies below that of a hole in the outer shell of  $\text{Cd}^{2+}$ , so the holes produced should move rapidly away from the PAC centre. Although a hole could subsequently be trapped on the lattice nearby, the lifetime of trapped hole states is typically much shorter than would be required to explain the PAC data of figure 1, of the order of 500 ns at 100 K. In any case, electronic after effects typically result in spectra quite different from those presented in figure 1 [15].

The simplest and most appealing interpretation is that the equilibrium structure of the point-defect complexes is dependent on the temperature, analogous to a phase change in bulk materials. In this model two configurations, perhaps having vacancies at nearest and next-nearest sites as proposed above, differ in energy by only a small amount. Differences in the entropy of the different configurations could then facilitate a crossover in the Gibbs free energy associated with the two structures, if the defect of higher enthalpy also has algebraically higher vibrational entropy. Note that this model does not involve a temperature dependence of either enthalpy or entropy, as these quantities are expected to change only at much higher temperatures. The relative probability of two configurations  $c_1$  and  $c_2$ , and hence the ratio of the fractions measured by PAC, is given by a ratio of Boltzmann factors

$$P(c_1/c_2) = \exp(S_1/k - h_1/kT) / \exp(S_2/k - h_2/kT) = \exp(\Delta S/k - \Delta h/kT). \quad (3)$$

The measured transition temperature and the width of the transition region allow an estimate of the parameters  $\Delta s$  and  $\Delta h$ , the differences in entropy and enthalpy, for the two configurations. This analysis is presented in figure 4, where equation (3) is plotted for values of  $\Delta s$  and  $\Delta h$  appropriate to the data. While there are actually several configurations involved and not just two as equation (3) implies, it is assumed that the configurations dominating at a given temperature are very close in energy, so that the data can be described approximately by a single transition. Figure 4 may therefore be thought of as representing the ratio  $(f_3 + f_4)/(f_1 + f_2)$ . The resulting estimates of the entropy and energy differences between the dominant high- and low-temperature configurations in both materials should therefore be interpreted as average differences between the low- and high-temperature

configurations. Note that this analysis predicts that the transition will not be complete over this temperature range, consistent with the data presented in table 1.

The entropy  $\Delta s$ , which mainly affects the width of the transition, is found to be  $5.7 \pm 0.5k_B$ . The imprecision of the estimate arises from the imprecision of this largely qualitative analysis. The enthalpy difference  $\Delta h$  is found to be  $64 \pm 5$  meV. These numbers are consistent with the fact that, in ionic crystals, defect vibrational entropies are typically found to be several times  $k_B$ , and enthalpy differences between nearest- and next-nearest-neighbour vacancy configurations are expected to be in the range of tens of meV.

The damping of the  $R(t)$  spectra in the transition region would appear to indicate *fluctuations at frequencies of the order of the quadrupole interaction frequencies,  $\sim 10$  MHz*. Assuming these fluctuations to be correlated with lattice vibrations, and using the Debye frequency as a prefactor, the energy barrier characterizing this process is found to be of the same order as  $\Delta h$ . We emphasize, however, that in the vicinity of a lattice defect the actual attempt frequency is expected to depend on local mode frequencies, which can vary greatly.

## 5. Concluding remarks

Previous theoretical and experimental work on crystals with the NaCl structure has shown that impurity complexes consisting of multivalent cations bound to nearest-neighbour cation vacancies or next-nearest cation vacancies are indeed often close in energy. Ionic thermocurrent measurements consistently reveal two peaks, which are attributed to configurations having nearest and next-nearest cation vacancies [16]. Likewise, EPR experiments in alkali and silver halides show that vacancies sometimes occupy next-nearest cation sites, and sometimes nearest cation sites, the preference depending to some extent on the size of the impurity [17, 18]. Theoretical calculations in alkali halides support this view [19]. If one accepts the speculation that the defects above the reversible transition involve vacancies at nearest Ag sites, then the present work takes this concept one step further, demonstrating that vacancies may occupy different sites at different temperatures, within the same material.

For sodium chloride, HADES simulations have predicted that the vacancy positions nearest and next nearest to the impurity ion differ in energy by about 10% of the total binding energy [20]. Since the binding energy for such complexes in the silver halides is known to be  $\sim 0.25$  eV per vacancy this result, if extended to silver halides, is consistent with the values obtained from the above thermodynamic analysis.

Most of the data available on the structure and behaviour of point-defect complexes have been obtained from techniques that are each useful only over a fairly narrow range of temperatures. EPR, for example, is ideal for determining defect structures at low temperature, but except in rare cases cannot be applied at higher temperatures. The ionic thermocurrent methods have even more severe temperature limitations: they are limited to the temperatures at which relaxation peaks appear. In contrast, PAC has no such limitation, and this has allowed it to provide a picture of the equilibrium behaviour of point-defect complexes over a broad temperature range.

A detailed analysis of the transition discussed in this paper is clearly desirable, with emphasis both on determining the defect structures in those cases where they are not already known, and also, once these structures are known, on modelling the transition more quantitatively. Ideally, one would calculate the perturbation function explicitly in the context of the proposed model and test its agreement with the data. Such an effort is underway.

## Acknowledgments

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## References

- [1] Baldereschi A, Czaja W, Tosatti E and Tosi M (ed) 1984 *The Physics of Latent Image Formation in Silver Halides* (Singapore: World Scientific)
- [2] Wichert Th and Recknagel E 1986 *Microscopic Methods in Metals (Springer Topics in Current Physics 40)* ed U Gonser (Berlin: Springer) p 317
- [3] Wichert Th and Swanson M L 1989 *J. Appl. Phys.* **66** 3026
- [4] Aepli H, Bishop A S, Frauenfelder H, Walter M and Züti W 1951 *Phys. Rev.* **82** 550
- [5] Austin J C, Swanson M L, Hughes W C, Kao C T, Slifkin L M, Höfssass H C and Frey E C 1990 *Phys. Rev. B* **42** 7699
- [6] Austin J C, Swanson M L and Hughes Wm C 1993 *Nucl. Instrum. Methods B* **73** 429
- [7] Frauenfelder H and Steffen R M 1965 *Alpha-, Beta-, and Gamma-ray Spectroscopy* ed K Siegbahn (Amsterdam: North-Holland) p 997
- [8] Winkler H and Gerdau E 1973 *Z. Phys.* **262** 363
- [9] Frisch J, Hense V and Wolf G 1973 *Ber. Bunsenges Phys. Chem.* **77** 513
- [10] Golapentia D A 1975 *Thesis* University of North Carolina at Chapel Hill
- [11] Stoneham A M 1975 *Theory of Defects in Solids* (Oxford: Clarendon) p 807
- [12] Eachus R S, Graves R E and Olm M T 1978 *J. Chem. Phys.* **69** 4580
- [13] Lidiard A B 1971 *Theory of Imperfect Crystalline Solids: Trieste Lectures 1971* (Vienna: International Atomic Energy Agency) p 364
- [14] Snell A H and Pleasonton F 1956 *Phys. Rev.* **102** 1419  
Baeverstam U, Othaz R, deSousa N and Ringstrem B 1972 *Nucl. Phys. A* **186** 500
- [15] Wang R, Gardner J A, Evenson W E and Sommers J A 1993 *Phys. Rev. B* **47** 639
- [16] Klien B J 1976 *PhD Thesis* University of North Carolina at Chapel Hill
- [17] Watkins G D 1959 *Phys. Rev.* **113** 79
- [18] Cook F B I and Smith M J A 1973 *J. Phys. C: Solid State Phys.* **6** 3785
- [19] Tosi M P and Fumi F G 1954 *Nuovo Cimento* **8** 584
- [20] Hayes W and Stoneham A M 1985 *Defects and Defect Processes in Nonmetallic Solids* (New York: Wiley)