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On the stability of the tetrahedral In-4V_{Ag} complex in silver halides

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Abstract. A point defect complex in silver chloride consisting of a trivalent iron ion in a cube-centre interstitial site, tetrahedrally coordinated with four silver vacancies and four halogen ions, was previously detected by EPR. In this article we present evidence, obtained by perturbed angular correlation spectroscopy, for a similar defect complex for In^{3+} in AgCl and AgBr. We present data establishing the existence of this negatively-charged complex, describe its behaviour, and consider why a negatively-charged complex forms.

1. Introduction

Manufacturers of practical photographic films often introduce trivalent cation impurities into silver halide emulsions to act as photocarrier traps in order to modify the film's properties [1]. Experiments show that trivalent impurities in AgCl and AgBr typically occupy substitutional sites. Electroneutrality requires compensation of the impurities' excess charge [2]; this generally occurs by the creation of two silver vacancies for each impurity ion. Many of these vacancies bind to the impurity ion (depending on the temperature and other factors) at nearest and next-nearest cation sites [3]. Interest in the structure of these impurity-vacancy centres arises because the number and arrangement of charge-compensating silver vacancies determines the impurity's photocarrier trapping behaviour.

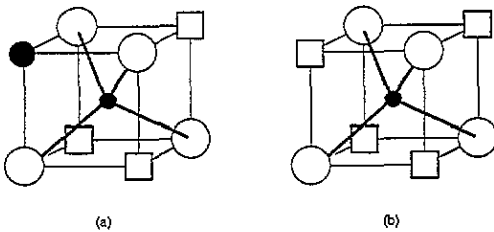


Figure 1. Interstitial M^{3+} defects in AgCl and AgBr. (a) The trigonal complex. (b) The tetrahedral complex. The small filled circles indicate M^{3+} ions; the larger filled circle indicates a Ag^+ ion; unfilled circles indicate halogen ions; unfilled squares indicate vacant silver sites.

Fe^{3+} is unusual among the well-characterized trivalent impurity ions in that it occupies an interstitial site, compensated either by three silver vacancies in a neutral, trigonal configuration (figure 1(a)) or by four silver vacancies in a negative-charged, tetrahedral configuration (figure 1(b)) [4–6].

In this article we report evidence, from perturbed angular correlation (PAC) spectroscopy, that a tetrahedral defect complex also exists for the ion In^{3+} in AgCl and AgBr . PAC measurements show that in certain AgCl and AgBr samples, held at temperatures between 126 K and 180 K for a period of at least several hours, a fraction of the In^{3+} ions move into sites of cubic symmetry. The formation of a tetrahedral defect complex is the only explanation for this phenomenon approximately consistent with the condition of electroneutrality. In light of the stability of the tetrahedral defect centre for the indium ion, an ion that is chemically quite different from the ferric ion, a reconsideration of the arguments regarding the stability of tetrahedral $M_{int}^{3+}4V_{Ag}$ defect centres is appropriate.

2. Experimental details

Detailed treatments of the PAC technique are abundant in the literature [7]. Here we provide a short description. PAC spectroscopy utilizes radiation from probe nuclei to measure the strength and symmetry of hyperfine interactions between those nuclei and their surroundings. PAC monitors the nuclear spin precession caused by the electric quadrupole interaction between a probe nucleus and the inhomogeneous electric field that arises from asymmetry in the charge distribution surrounding the probe nucleus. When such asymmetries exist, the precession of the nuclear spin causes the anisotropic nuclear radiation pattern to precess; this precession is observed by measuring two gamma rays in coincidence as a function of angle and time. The ratio $R(t)$ directly displays the time-dependence of the angular correlation between the two gamma rays resulting from this precession. Of particular interest to the present article is the case where probe ions occupy sites of cubic symmetry; in this case the EFG vanishes, the nuclear radiation pattern does not depend on time, and the contribution of those probe ions to $R(t)$ is time-independent. Configurations of cubic symmetry are therefore easy to distinguish from configurations of less-than-cubic symmetry.

Measurements were made on a variety of powder and single-crystal AgCl and AgBr samples. Powder samples were obtained commercially and, in some cases, purified by Mr Charles Childs. Single crystals were grown in this laboratory by Mr Childs, using the Bridgman method and highly purified starting materials. Single-crystal samples were etched in sodium thiosulphate to remove surface contamination and relieve surface strain. All samples were sealed in HF-etched quartz ampoules with a small amount of $^{111}\text{InCl}_3$ and a fraction of an atmosphere of Cl or Br gas. They were then annealed slightly below the melting temperature for a period of hours or days in order to diffuse the indium probe ions into the sample. Measurements utilized a standard fast-slow coincidence spectrometer with four sodium iodide detectors. During PAC measurements, the temperature was maintained constant to within 2 K using a closed-cycle liquid helium refrigeration system. Anneals below room temperature were also made in this refrigerator, and the cooling rate was determined by the maximum rate achievable in this system which, though dependent on the temperature, was typically about ten degrees per minute. Unless otherwise noted, all measurements and anneals were carried out in the dark.

A very small number of probe ions is needed for a PAC measurement; the concentration of probe ions in a typical sample is well below the concentration of accidental contaminants, even in pure samples. Because ^{111}In decays to ^{111}Cd , the concentration of Cd always exceeds the concentration of ^{111}In . As a result of these two factors, indium is always a minority impurity unless the sample is intentionally doped by a larger concentration of stable indium.

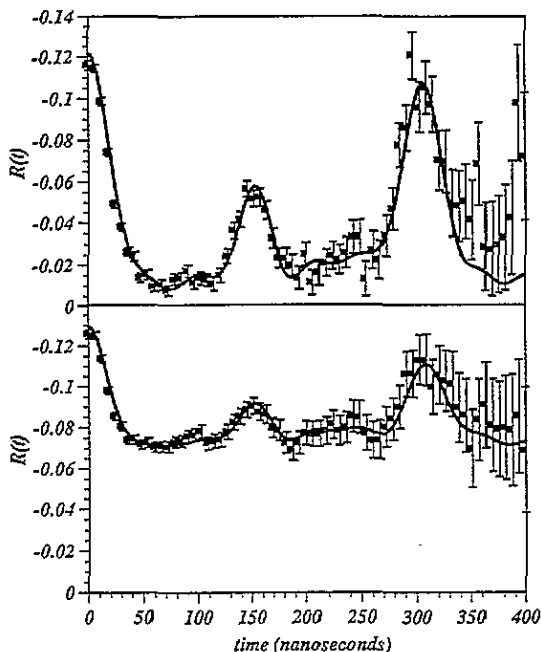


Figure 2. PAC spectra indicating the formation of the tetrahedral defect complex for the In^{3+} ion in AgCl. The top panel shows $R(t)$ for AgCl doped with ^{111}In probe ions, measured at 77 K. The bottom panel shows $R(t)$ measured at the same temperature after annealing for several hours at 180 K. The increase in the baseline indicates an increase in the number of indium ions in cubic-symmetric sites.

3. Results and discussion

3.1. Evidence for the existence of the tetrahedral defect

Figure 2 shows two PAC $R(t)$ spectra for AgCl:In held at 77 K, measured under identical conditions, the first preceding a four-hour anneal at 180 K, the second immediately following this anneal. The spectrum of figure 2(a) is typical of the AgCl:In system below 120 K. This spectrum consists of two triplets of three frequencies, indicating two main configurations for the indium-vacancy complexes, both consisting of a single trivalent indium ion on a Ag site and two vacancies bound at next-nearest Ag sites. These two complexes differ only in the relative position of the silver vacancies: one has vacancies at right angles, and the other has vacancies on opposite sides of the indium ion. Analysis of the structure of these defects was detailed in other articles and will not be discussed here [8, 9].

The spectrum of figure 2(b) shows that after the anneal these two complexes still exist, but in smaller numbers: the fraction of indium probe ions in these complexes is reduced. This reduction is compensated by growth in the fraction of probe ions in sites of cubic symmetry. This is shown by the increase in the $R(t)$ base line from about -0.01 in figure 2(a) to about -0.075 in figure 2(b), which represents a large increase in the time-independent component (or cubic symmetry component) of the spectrum. In this case the 180 K anneal caused over half the In atoms to occupy cubic symmetry sites. The details of this conversion varied dramatically from sample to sample: in some samples the conversion occurred at

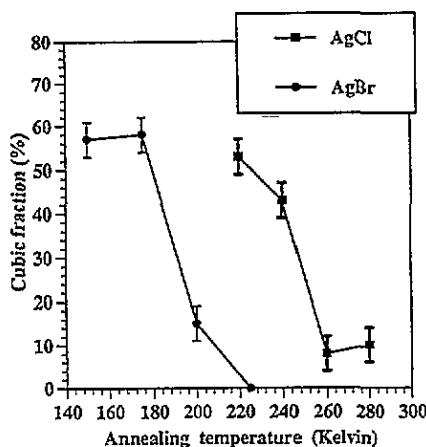


Figure 3. The reduction in the fraction of indium ions in cubic-symmetric sites for AgCl (filled squares) and AgBr (filled circles).

temperatures as low as 126 K; in others, temperatures of 180 K were required. In still others the conversion was never seen.

There is no fully charge-compensated complex having cubic symmetry about the site of a trivalent probe ion on the rocksalt lattice. An uncompensated indium ion on a Ag site has a net charge of +2, and the complex shown in figure 1(b), consisting of an indium ion in a cube-centre interstitial site tetrahedrally coordinated with four Ag vacancies and four halogen ions has a net charge of -1. The uncompensated indium ion is improbable, since these indium-vacancy complexes are stabilized by a Coulomb attraction of the order of 1 eV. We have experimental evidence contradicting the hypothesis of the uncompensated substitutional indium ion: when AgBr samples were heated above 200 K, the fraction of indium ions in cubic-symmetric sites declined dramatically (figure 3). After several hours the fraction of probe ions in cubic-symmetric sites approached zero. Annealing above this temperature restored the indium-divacancy complex, as observed by subsequent PAC measurements at low temperatures.

The same behaviour was seen in AgCl, but at a higher temperature: the cubic-symmetric defect fraction was reduced upon annealing about 250 K (figure 3). Above this temperature, dynamic effects dominated the PAC spectra, obscuring detailed structural information, but it is clear that the indium ion no longer occupies a cubic-symmetric site. The rate and character of these dynamic effects are consistent with the diffusion of bound silver vacancies between equivalent sites adjacent to the indium probe ion [10]. When the sample was subsequently cooled to lower temperatures, the usual indium-divacancy complexes were restored. At least one silver vacancy must still have been bound to the probe ion in the cubic symmetric configuration if the higher temperature behaviour is to be explicable. This rules out the hypothesis of the uncompensated substitutional indium ion. The tetrahedral defect complex of figure 2(b) is the only reasonable alternative.

There is other evidence supporting this hypothesis. Since an extra vacancy is required to form the tetrahedral complex from the fully compensated, charge-neutral species, changes in the free vacancy concentration are likely to affect the rate at which the tetrahedral complex is formed. When Cd (or another divalent cation) is added to the crystal, additional silver vacancies are formed to maintain the crystal's charge neutrality. There is typically some degree of association between the impurity and its charge-compensating vacancy, but at

finite temperatures some fraction of the vacancies will be free. Hence, increasing the concentration of polyvalent cations typically increases the free vacancy concentration [2]. Since the concentration of indium probe ions is of the order of 10 ppb, far below the level at which contamination can be controlled, changes in the impurity concentration arising from minor, unintentional variations in sample purity and preparation procedures can significantly affect the rate of the conversion.

One would expect an intentional change in the concentration of multivalent cation impurities to influence the rate and temperature at which the conversion occurs, since the concentration of free cation vacancies determines the probability of encounter between an impurity complex and a free vacancy at a given temperature.

We have not made a systematic study of the effect of impurity concentration on the rate and temperature of the conversion, but we did make measurements on a sample doped during growth with about 100 ppm of Cd^{2+} . When introduced onto the AgX lattice, Cd^{2+} causes the formation of additional silver vacancies to compensate the impurity's excess charge. At finite temperature some fraction of these vacancies will dissociate from the Cd^{2+} ion, resulting in an increased free vacancy concentration. Figure 4 shows partial results of an isochronal annealing sequence for AgCl doped with 100 ppm Cd. In this sample the formation of the tetrahedral defect began at 126 K, the lowest conversion temperature seen in any sample. This temperature is roughly consistent with the onset of vacancy diffusion, as determined from ionic thermocurrent measurements and extrapolated from mobility measurements made at higher temperatures [11].

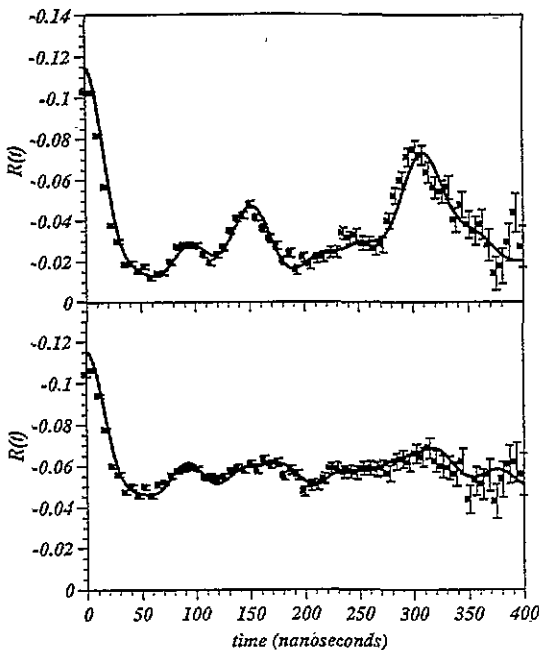


Figure 4. The formation of the tetrahedral complex in AgCl doped with 100 ppm Cd. The top panel shows a typical low-temperature measurement; the bottom panel shows a measurement made at 127 K. The figure shows an increase in the fraction of indium ions in the tetrahedral defect at a particularly low temperature in Cd-doped material, where the free vacancy concentration is high.

In summary, the evidence suggests that the increase in the fraction of indium ions in cubic-symmetric sites is caused by the formation of the tetrahedral complex of figure 1(b), as was reported for the ferric ion in [4–6]. This complex is probably formed when a diffusing free vacancy encounters a neutral indium ion–vacancy complex; this free vacancy is then trapped at a Ag site adjacent to the In^{3+} ion and the tetrahedral complex of figure 1(b) is formed.

3.2. On the stability of the negatively-charged tetrahedral defect complex

A similar tetrahedral complex has been observed by EPR for the ferric ion. Several authors reported a defect of tetrahedral symmetry about an Fe^{3+} impurity in AgCl [4–6]. In order to explain why formation of the negatively-charged $\text{M}_{int}^{3+}4\text{V}_{Ag}$ defect is favourable, Hayes *et al* [4] and Laredo *et al* [6], invoked the particular character of the $\text{Fe}^{3+}\text{--Cl}^-$ bond. Their explanations are not directly applicable to In^{3+} ; a reconsideration of the stability of this overcompensated complex is thus appropriate.

We believe that the stability of the negatively-charged tetrahedral defect centre is explicable on purely ionic grounds, if a sufficient concentration of free vacancies is already present in the sample. As we have mentioned, multivalent cation impurities are charge-compensated by the creation of Ag vacancies, some of which will be uncomplexed at finite temperature. It is possible that complex formation between these negatively-charged vacancies and a neutral defect centre could be energetically favourable. For example, it is reasonable that the reaction between the trigonal defect centre (figure 1(a)) and a free vacancy, forming the tetrahedral complex (figure 1(b)) ($\text{In}_{int}^{3+}3\text{V}_{Ag}^{1-} + \text{V}_{Ag}^{1-} \rightarrow \text{In}_{int}^{3+}4\text{V}_{Ag}^{1-}$) would be favourable, since this reaction allows the Ag^+ ion and the In^{3+} ion to move further apart. One may consider a negatively-charged tetrahedral defect as replacing an uncomplexed silver vacancy as the species compensating the excess positive charge of a Cd^{2+} ion. If vacancies do not already exist in adequate numbers, they would have to be created at a prohibitive cost in energy in order to form the tetrahedral complex. One therefore expects to see such complexes only in materials having a substantial concentration of free vacancies.

3.3. Details

In some AgBr and AgCl samples, the cubic-symmetric fraction did not increase in the earliest measurements, but did increase later, after an interval of days or weeks, usually after the sample had been doped several times with fresh ^{111}In activity. This phenomenon probably arises from one or both of two factors: each time the sample is doped and annealed the opportunity exists for new contamination by environmental impurities; in particular, we note that the InCl_3 solution typically will contain non-radioactive impurities exceeding the number of ^{111}In ions. It is also notable that ^{111}In decays to ^{111}Cd , so the concentration of Cd increases gradually, perhaps increasing enough that the concentration of charge-compensating Ag vacancies allows the creation of tetrahedral defects in measurable quantity.

In some samples where the conversion occurred in the initial experiments, it no longer occurred after the sample was annealed at room temperature for a number of hours. This would seem to indicate that annealing at room temperature causes a reduction in the free vacancy concentration. This might be caused, for example, by the precipitation of multivalent impurities into clusters, reducing the concentration of free silver vacancies.

All the phenomena described so far occurred in AgCl and AgBr. The behaviour of the tetrahedral defect in the two materials was in most respects very similar, but there were

some important differences. In general, the transition occurred at lower temperatures in AgBr than in AgCl, although the considerable sample-to-sample variation makes it difficult to say whether this difference is intrinsic. If it is, then it would indicate greater vacancy mobility, a larger vacancy concentration, or greater stability of the tetrahedral defect in AgBr than in AgCl.

We have already mentioned that the AgBr tetrahedral complex vanishes on annealing to 200 K, while the AgCl complex is stable up to about 250 K. As figure 2 indicates, once the tetrahedral defect is formed in AgCl, it remains as long as the temperature stays below 250 K. In AgBr the situation is quite different: the fraction of indium ions in cubic-symmetric sites vanishes *both* at higher temperatures *and* at lower temperatures. This behaviour is illustrated in figure 5, which shows $R(t)$ for measurements made at 12 K (top), 180 K (middle), and again at 12 K (bottom). The baseline of $R(t)$ is substantially larger in the 180 K measurement than in the previous 12 K measurement, about -0.06 as compared to -0.015 . When the 12 K measurement is repeated, the baseline is once again reduced, to about -0.02 . This indicates that the fraction of indium atoms in cubic-symmetric sites increases from 24% in the first 12 K measurement to about 60% in the 180 K measurement; in the second 12 K measurement the fraction of indium atoms in cubic-symmetric sites declines again to 30%.

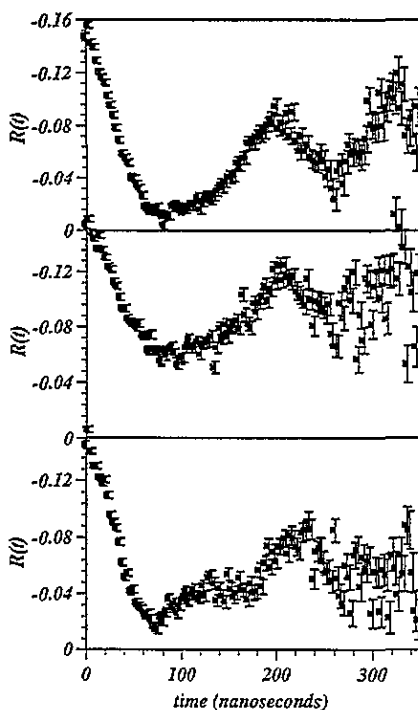


Figure 5. The tetrahedral defect in AgBr. The top panel shows $R(t)$ for AgBr at 12 K; the middle panel shows $R(t)$ at 180 K; the bottom panel shows $R(t)$ for a subsequent measurement at 12 K. Notice that the baseline, corresponding to the fraction of indium ions in cubic-symmetric configurations, increases on annealing at 180 K, then decreases again when the temperature is lowered again to 12 K.

While in AgCl this conversion can be understood as an annealing effect, the system accessing a new, lower-energy configuration, given sufficient time and temperature, this

cannot explain the temperature-reversible transition seen in AgBr. We do not yet have a satisfactory explanation for this difference between AgCl and AgBr. This reversibility would seem to indicate that the stability of the tetrahedral defect is temperature-dependent; i.e., that the tetrahedral complex is only stable at the higher temperature. This may indicate a thermal equilibrium between the tetrahedral defect and some other vacancy trap. Another possible explanation is that vibrational entropy effects cause the relative stability of two configurations to vary with temperature, not unlike the reversible structural transitions observed in AgCl between 130 K and in AgBr at 90 K. This phenomenon is analysed in one published article [12] and one forthcoming article [9].

4. Summary

We observed, in some AgCl and AgBr samples, an increase in the fraction of $^{111}\text{In}^{3+}$ ions in cubic-symmetric sites. The rate and temperature at which this conversion occurred varied from sample to sample. There is only one attribution for this cubic-symmetric defect centre that is consistent with what is known about the behaviour of such systems: the negative-charged configuration shown in figure 1(b). We have argued that the stability of this defect is explicable on purely ionic grounds. In both AgCl and AgBr, the tetrahedral defect vanished at higher temperatures, 250 K for AgCl and 200 K for AgBr. In AgCl the tetrahedral defect remained when the temperature was lowered to below the formation temperature, but in AgBr lowering the temperature caused the defect centre to revert back, at least partially, to the usual low-temperature configuration. This represents yet another example of a surprising number of qualitative distinctions between the behaviour of defects in these very similar materials.

Acknowledgments

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