

## Letters to the Editor

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### Interstitialcy Diffusion Mechanism in Silver Chloride

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(Received March 16, 1956)

RECENT work by Compton<sup>1</sup> and Friauf<sup>2</sup> indicates the failure of the Einstein relation in the silver halides when the tracer diffusion constant is used. McCombie and Lidiard<sup>3</sup> show that this can be reasonably well explained if the  $\text{Ag}^+$  migrates by the interstitialcy mechanism (whereby the interstitial displaces a like lattice ion which then becomes an interstitial), although apparently contributions from noncollinear processes must be assumed. Since rather careful

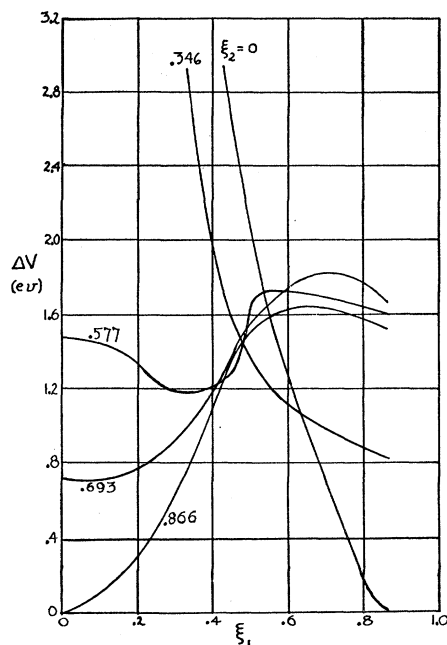


FIG. 1. Energy contours for noncollinear interstitialcy migration in AgCl (rigid lattice).

calculations of the activation energies for both a noncollinear and a collinear interstitialcy process have been carried out,<sup>4</sup> it appears worthwhile to present the results of the computation, especially in view of the above

interest. Unlike the simpler migration models, the saddle point for this mechanism is not known *a priori* since two ions are moving simultaneously. The general procedure followed in the computations was to fix the location of one ion and find the stable position of the other ion which minimized the total energy of the two ions. This was then done for several locations of the first ion. The activation energy is the difference between the energy of the complex in its highest activated state and in the initial state (assumed to be a silver ion in the center of the smallest lattice cube). As a silver ion moves from a cube center location to a silver-ion lattice site, it approaches most closely to the three chlorine ions, lying in a (111) plane, at one-third the total path length. The saddle point for the process may be expected to occur when one silver ion is in this position of closest approach to the three chlorine ions and the other silver ion nearly so (in an adjacent cell, of course). Thus the relaxation of these six chlorine ions (three for each silver ion) will be the most significant contribution of lattice relaxation to the activation energy, and can be found by a comparatively simple calculation. The procedure followed, then, in the present computation was to obtain the energy contours, hence the activation energy, for a rigid lattice and then correct this by the amount of the relaxation energy discussed above. The interactions considered were the Coulomb energy (both due to the mutual interaction of the two moving positive ions and the negative empty lattice site and to the rest of the lattice), the repulsive overlap and attractive van der Waals energies (using the semiempirical expressions given by Mayer<sup>5</sup>) and the lattice polarization energy (using lattice polarizabilities, for the  $\text{Ag}^+$  ion, the  $\text{Cl}^-$  ion and the displacement, of  $1.61 \text{ \AA}^3$ ,  $3.46 \text{ \AA}^3$ , and  $1.98 \text{ \AA}^3$  as computed from the dielectric constants). The contribution of long-range lattice polarization to the activation energy can be shown to be negligible, but the dipole moment induced on each of some thirteen nearest neighbors was computed for each configuration of the two interstitialcy ions.

The energy contours were calculated in detail for the noncollinear case where the lattice ion moves into an adjacent cell having one edge in common with the original cell. These contours are shown in Fig. 1, where the coordinates  $\xi_2$  and  $\xi_1$  are normalized to the interionic spacing of  $2.77 \text{ \AA}$ , have a common origin at the lattice site of the ion to be displaced, and point normal to the (111) planes of the initial and the future interstitial cells. Then as the original interstitial moves toward the corner lattice site, its coordinate ( $\xi_2$ ) goes from 0.866 to zero. Each curve in Fig. 1 is thus the energy change of the system for a fixed interstitial position ( $\xi_2$ ) as a function of the position of the erstwhile lattice ion ( $\xi_1$ ). The minimum in a given curve locates the stable position of the lattice ion and hence the total energy of the system for this interstitial site. Thus, for  $\xi_2=0.577$ , the interstitial is closest to the three (111)-plane chlorine ions and the lattice ion is displaced to  $\xi_1=0.346$ ,

not quite up to the plane of its three chlorine neighbors. If the interstitial is held at  $\xi_2=0.346$ , the system energy must be the same, when the lattice ion is at  $\xi_1=0.577$ , as for the above case, but of course this is not a stable position of the lattice ion which would prefer to go all, or almost all, the way down to its new interstitial site. The saddle point for the process was taken to be  $\xi_2=0.577$ ,  $\xi_1=0.346$ , giving a preliminary activation energy (from Fig. 1) of 1.2 ev. The lattice relaxation reduces this by 0.4 ev, so that the final activation energy is 0.8 ev. For a collinear path the only major difference from the above noncollinear case lies in the mutual interaction of the two moving ions. For the above saddle point coordinates, this correction to the energy change was found to be  $(-0.82)$  ev for the collinear mechanism, indicating practically a zero "activation energy." However, for the symmetrical case of  $\xi_1=\xi_2=0.346$ , the energy difference from the conventional interstitial site was found to be  $(-0.17)$  ev, which would indicate that the stable interstitial state requires the two silver ions to form a dumbbell arrangement about a (111) plane containing all silver ions. Even if the errors of assumption are sufficient to invalidate this model, the activation energy for the collinear process will certainly be much less than that for the noncollinear. It should be mentioned that the activation energy for the process whereby the interstitial migrates through a cell face (where lattice distortion is very important) was also computed. Since its value was over 3 ev, this mechanism cannot compete with interstitialcy migration.

The writer is happy to acknowledge valuable discussions of these points with J. A. Krumhansl and D. R. Westervelt.

<sup>1</sup> W. D. Compton, Phys. Rev. **101**, 1209 (1956).

<sup>2</sup> R. J. Friauf, Bull. Am. Phys. Soc. Ser. II, **1**, 145 (1956).

<sup>3</sup> C. W. McCombie and A. B. Lidiard, Phys. Rev. **101**, 1210 (1956).

<sup>4</sup> These form a portion of the writer's Ph.D. thesis, Cornell University, 1953 (unpublished).

<sup>5</sup> J. Mayer, J. Chem. Phys. **1**, 330 (1933).

## New Materials for Magnetic Cooling and Thermometry below 1°K

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(Received March 5, 1956)

A MAJOR drawback to the use of the familiar hydrated inorganic salts, e.g., the alums, for work in the temperature range below 1°K is their inherent instability, i.e., a tendency to lose part of their water of crystallization, with resultant modification of magnetic properties. It also seems likely that the renowned discrepancies between absolute temperature deter-

minations with the same substance in different laboratories<sup>1</sup> are in part due to such instability.

Suggestions have recently been made that water-free paramagnetics such as ferric acetyl-acetonate<sup>2</sup> or certain inorganic oxides (e.g.,  $\text{Al}_2\text{O}_3$ ) containing para-

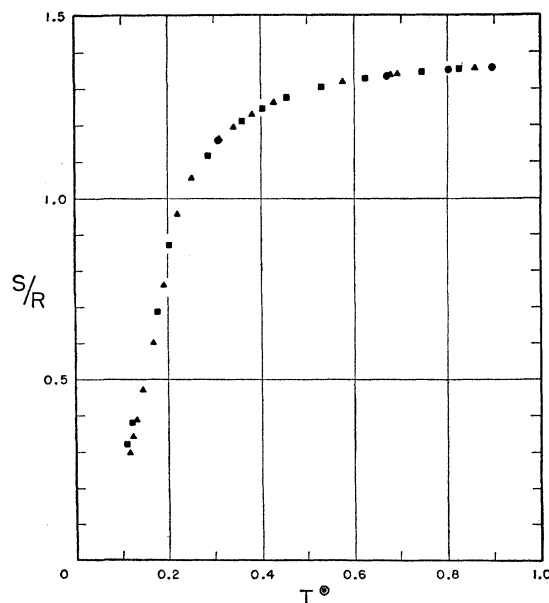


FIG. 1. Entropy as a function of magnetic temperature for ammonium hexafluorochromite,  $(\text{NH}_4)_3\text{CrF}_6$ . The different symbols refer to data obtained on three successive days.

magnetic impurities,<sup>2,3</sup> might provide a satisfactory solution to the problem. The writers wish to draw attention to the possibilities of another class of substance, viz., paramagnetics of the  $(\text{NH}_4)_3\text{FeF}_6$  structure. A study of this group was initiated more than a year ago in this laboratory with some preliminary investigations into the properties of ammonium hexafluorochromite,  $(\text{NH}_4)_3\text{CrF}_6$ , but since it was found necessary to set this program aside temporarily it was thought worthwhile to publish the findings to date.

Some exploratory paramagnetic resonance investigations on the powder<sup>4</sup> had indicated that the crystalline electric field splitting,  $\delta$ , of the  $\text{Cr}^{+++}$  ion in this salt is somewhat greater than in the chromic alums. Adiabatic demagnetizations from about 1.2°K in fields of up to 23 kilogauss using a spherically-shaped powder-specimen yielded the results shown in Fig. 1. The entropy,  $S$ , was calculated on the assumption of an isotropic  $g$ -value equal to 2, the (small) corrections due to the effects of the crystalline electric field being crudely calculated through direct analogy with the behavior of the chromic alums.<sup>5,6</sup>

In the region just below 1°K the points fit a curve given by  $(\ln 4) - S/R = A(T^*)^{-2}$ , where  $R$  is the gas constant and  $A=0.0232$ . From this, allowing 0.0030 for the dipole-dipole contribution<sup>7</sup> to  $A$ , we derive the value