

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 interstitial migration.

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

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 These form a portion of the writer's Ph.D. thesis, Cornell University, 1953 (unpublished).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

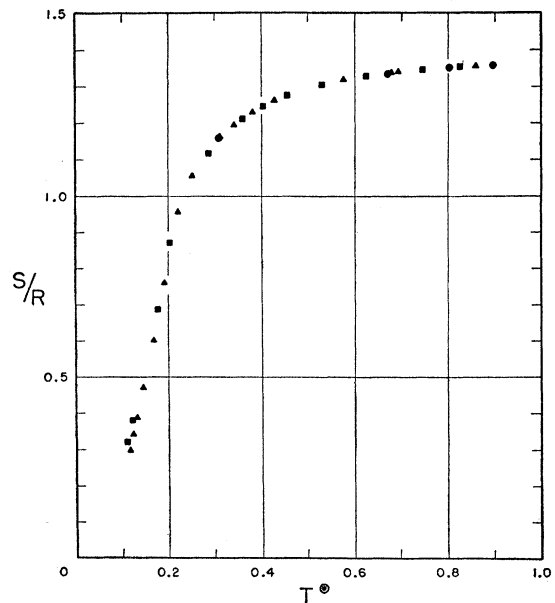


FIG. 1. Entropy as a function of magnetic temperature for ammonium hexafluorochromite,  $(\text{NH}_4)_3\text{CrF}_6$ . The different symbols refer to data obtained on three successive days.

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

0.40 degree ( $0.28 \text{ cm}^{-1}$ ) for  $\delta/k$ . With this value of  $\delta$  the salt should exhibit a maximum in the specific heat,  $C$ , in the region of  $0.16^\circ\text{K}$  while in the "high" temperature region, where  $C \propto T^{-2}$ ,  $C/R$  is about twice that of chrome alum. Since, moreover, the molar volume is some 2.5 times smaller than that of chrome alum,<sup>7</sup> the heat capacity *per unit volume* (which is the important quantity from the more practical point of view) is 5 times greater.

The theory of Hebb and Purcell<sup>8</sup> as developed for the alums when applied to this salt describes the observed behavior only approximately (as might be expected). The fit is good down to  $T^*=0.4^\circ$ , below which the entropy falls off more and more rapidly than is predicted by the theory. It is interesting to note, however, that no maximum in the susceptibility was observed down to the lowest entropy obtained in these experiments ( $S/R=0.3$ ).

This work will be continued and extended to other members of the isomorphous series, e.g.,  $(\text{NH}_4)_3\text{FeF}_6$ ,  $\text{K}_3\text{FeF}_6$ , etc. The authors are indebted to Dr. L. S. Singer, then at the Naval Research Laboratory, for originally arousing their interest in the ammonium salt described above and for communicating his paramagnetic resonance results to them prior to publication.

<sup>1</sup> See, for example, E. Ambler and R. P. Hudson, Repts. Progr. Phys. 18, 251 (1955).

<sup>2</sup> J. G. Daunt and W. L. Pillinger, Conférence de Physique des basses températures, Paris, September 2-8, 1955, Commun. No. 18 (Suppl. au Bull. de L'I.I.F., p. 158).

<sup>3</sup> C. V. Heer and C. J. Rauch, Commun. No. 25, p. 218 of reference 2.

<sup>4</sup> L. S. Singer (private communication).

<sup>5</sup> R. P. Hudson, Phys. Rev. 88, 570 (1952).

<sup>6</sup> J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London) A221, 243 (1954).

<sup>7</sup> The structure of this salt is described by R. W. C. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Chap. IX. The chromic ions are situated on a face-centered cubic lattice,  $a_0=9.0 \text{ \AA}$ . In the alums the magnetic ions are similarly placed, with  $a_0=12.2 \text{ \AA}$ . The contribution to the entropy reduction due to dipole-dipole coupling is conveniently expressed in terms of a parameter  $\tau$  [see J. H. Van Vleck, J. Chem. Phys. 5, 320 (1937), Eqs. (18), (20), and (35)]; we find  $\tau=0.05$ . The possibility of a significant exchange interaction was discounted for the reason that the salt obeyed the simple Curie Law very closely in the liquid He region.

<sup>8</sup> M. H. Hebb and E. M. Purcell, J. Chem. Phys. 5, 338 (1937).

## Ionospheric Effects Produced by Solar Flare Radiation

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(Received February 8, 1956)

WITH reference to a recent paper by Sedra and Hazzaa,<sup>1</sup> there is now overwhelming evidence that ultraviolet radiation from solar flares does not affect the ionic density of the  $E$  and  $F1$  layers to any marked extent except perhaps in extremely rare cases.<sup>2</sup>

The "ion cloud," if such a term may be used, produced by the ultraviolet radiation from a solar flare extends over the entire sunlit hemisphere, and is at a height less than 100 km—not at 200 km as suggested by the authors. The 1929 Maris and Hulburt paper referred to was written at a time when the heights of the ionospheric layers, as well as their ion densities, were not regularly measured, and the solar flare effects on the ionosphere could only be guessed at.

The authors' illustration of a geomagnetic crochet is not typical. The interpretation of the ionospheric record shown in the paper is puzzling in that the "cloud" appearing at a virtual height of 200 km is either transparent (allowing reflections from the  $F2$  layer to reach the receiver), or what is more likely, it is a sporadic  $E$  cloud located off the zenith at a height of about 100 km giving a recorded slant range of 200 km. In either case, it is probably not possible to determine a critical frequency (or an ion density) for such a "cloud."

Although the paper deals with solar flare radiation, solar observational data are not given. So far as can be determined (it is not clear whether the times listed are local or Greenwich), no solar flares were observed anywhere else on the dates and near the times listed. Further, no magnetic crochets (solar flare effects) are given in the IATME Bulletins<sup>3</sup> for the dates and times listed.

<sup>1</sup> R. N. Sedra and I. B. Hazzaa, Phys. Rev. 99, 1070 (1955).

<sup>2</sup> W. Dieminger and K. H. Geisweid, J. Atm. and Terrest. Phys. 1, 42 (1951).

<sup>3</sup> IATME Bulletin 12h, Geomagnetic Indices, K and C, 1953; IATME Bulletin 12i, Geomagnetic Indices, K and C, 1954.

## Paramagnetic Resonance in As-Doped Silicon

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(Received March 12, 1956)

EXPERIMENTS involving long relaxation times in As-doped Si have been previously reported.<sup>1</sup> The experiments had been interpreted as suggesting a large spin polarization of the As donor nuclei. Further studies carried out on an equipment similar to the first, and on the same silicon sample containing  $1.3 \times 10^{17} \text{ As/cm}^3$ , lead us to believe that most of the effects previously observed, as well as some new effects, can be more satisfactorily explained on the basis of a long electronic relaxation time and accompanying adiabatic rapid passage behavior.

One way in which it was directly established that the 16-second relaxation time, previously attributed to the