Magnetic Polarizations of Electrons at Dislocations in Alkali Halides*

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A new ferromagnet has been discovered in the alkali halides. The temperature dependence of the permanent magnetic moment agrees with the Bloch spin-wave theory, $M=M_0[1-(T/T_c)^{3/2}]$, between 2 and 290°K. A calculation of the Curie temperature T_c gave (462±1)°K for two samples of NaCl and 545°K for a sample of KCl. The magnitude of the magnetization M_0 at 0°K can be accounted for by 10^{14} electrons per cm³. We believe all these electrons are trapped along dislocations and are responsible for the magnetic behavior described. These very pure single crystals of alkali halides contain a few parts per million of ferric ions, but they typically have some 10^6 dislocations per cm² which arise during growth from the melt. The experiments on the permanent magnetic moment show first an increase with soft x irradiation and then a decrease until the moment vanishes. The interpretation is that x irradiation excites electrons to the conduction band where they move until trapped to a depth of some 0.25 eV at dislocations. The number of electrons at first is small and the electrons may have parallel spins (Hund's rule), but as the number increases the ferromagnetic state is destroyed.

INTRODUCTION

THE experimental evidence for spin waves in alkali halides has been reported by this laboratory.[1] The details of the observed permanent magnetic moment and the convincing evidence that electrons trapped at dislocations were the source of the magnetic moment required further research. The present paper reports the findings which support these views.

The alkali halides are well known to be diamagnetic, and the crystals studied in this entire work are diamagnetic with values of the susceptibility in agreement with the literature. What is new in the magnetic studies reported here is that an extremely sensitive magnetometer—i.e., a torsion pendulum consisting of a cylinder of a very pure,[2] single-crystal alkali halide—permits the observer to measure very small permanent magnetic moments without disturbance from the gross diamagnetism. The electrons responsible for diamagnetism give no torque or damping action to the torsion pendulum when placed in a uniform magnetic field.

The experiments reported in this paper give the temperature dependence of the small permanent magnetic moment caused by the few electrons which are trapped on the dislocations found in most of these optical-quality, pure, single-crystal alkali halides. From these observations a calculation of the Curie temperature has been made and the agreement with the Bloch spin-wave theory confirmed. In addition the effect of soft x irradiation, under controlled conditions, has led to interesting new results which are reported. As long as scientists seek a microscopic understanding of ferromagnetism, new ferromagnets of the type reported here will be interesting possibilities for a fresh approach.

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[1] T. W. Adair, III, E. J. Sharp, and C. F. Squire, J. Chem. Phys. **44**, 3650 (1966).

[2] Harshaw research laboratories report typically only a few parts per million of ferric ion and no observable nickel or cobalt ions. Silicates are the dominant impurity.

EXPERIMENTAL RESULTS

Figure 1 shows a schematic drawing of the sensitive torsion pendulum, cryostat, and magnet which permitted torque measurements from which the magnitude

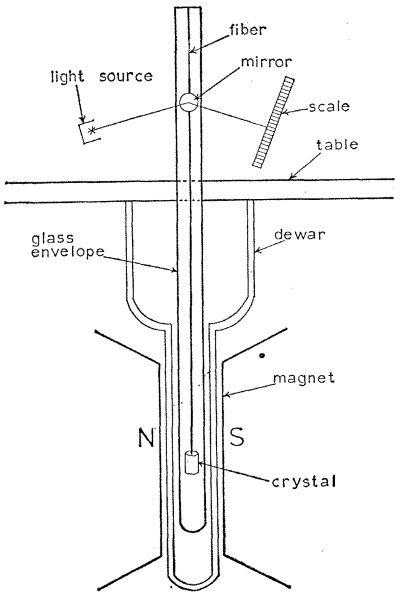

FIG. 1. Schematic drawing of the very sensitive magnetometer and cryostat used for the magnetic measurements. One mm deflection of the light beam on the scale arises from a torque of 1.5×10^{-4} dyn cm.

of the permanent magnetic moment may be calculated. The cylindrical single crystal of an alkali halide was suspended along its axis to form a sensitive torsion pendulum, and the crystal was in a uniform transverse magnetic field. The sample temperature was fixed by a cryogenic liquid in the Dewar flask which varied from 1.8°K (liquid helium), 78°K (liquid nitrogen), 88°K (liquid argon), 184°K (liquid ethane), and room temperature. The magnet used in this work was a Harvey-Wells, 12-in. pole diam, uniform field magnet of the type used in NMR experiments. A torque of 1.5×10^{-4} dyn cm caused a deflection of 1 mm on the scale shown in Fig. 1. The cylindrical sample was typically

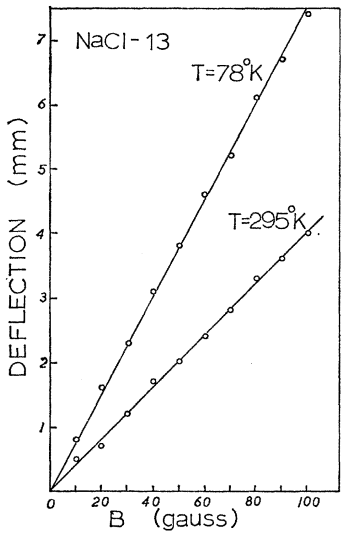

FIG. 2. Torque versus applied magnetic field for NaCl-13 at two different temperatures, 78°K and 295°K.

1.91 cm in diam by 2.54 cm long. They were supplied by Harshaw Chemical Company and by Optovac Company.

Two samples[3] of sodium chloride and one of potassium chloride were measured in the following manner. The crystals, having at the outset no magnetic moment, were magnetized in a 5000-G applied field at the temperature at which the crystals were to be measured. The magnetic field was then reduced to zero, leaving the permanent moment aligned with its maximum value in the direction of the previously applied 5000-G field. The magnet was then rotated 90° on its pedestal so that the small measuring field and the permanent moment were perpendicular to one another.

Measurements of the deflection were then made on the sample for values of the applied field from 0–100 G in increments of 10 G. Figure 2 gives the deflection-versus-field measurements for sodium chloride sample No. 13 (NaCl-13). A very good straight line can be drawn through the experimental points in both the room-temperature case and the 78°K case. This type of measurement was carried out at five different temperatures for NaCl-13. Similar measurements were made on two other samples, NaCl-7 and KCl-6, at three different temperatures.

Since these measurements are a linear function they permit the calculation of the permanent moment M_f at each temperature, from the equation $\tau=\mathbf{M}_f\times\mathbf{B}$, where τ is the torque exerted on the crystal by the applied field B.

The magnitude of the permanent moment was obtained for all three specimens at liquid helium (1.8°K), liquid nitrogen (78°K), and room temperature, and for NaCl-13 at two additional temperatures, liquid argon (88°K) and liquid ethane (184°K). The results of these experiments for NaCl-13 are given in Fig. 3 where we have plotted the normalized permanent moment against the normalized temperature. The solid line in Fig. 3 is a calculated curve using Bloch's equation[4] predicting the temperature dependence of the permanent moment, $M=M_0[1-(T/T_c)^{3/2}]$.

Table I gives the results for all three samples used in these experiments. For NaCl-13 we obtained a Curie temperature of 463°K with an M_0 of 12.95×10^{-9} Am^2, while for a different sample of sodium chloride, NaCl-7 we obtained a Curie temperature of 461.8°K with an M_0 of 8.83×10^{-9} Am^2. A sample of KCl gave a Curie temperature of 545.4°K for an M_0 of 11.53×10^{-9} Am^2.

For the helium temperatures a modification of the apparatus shown in Fig. 1 had to be made because of the lack of space between the pole faces of the magnet. The glass envelope was replaced by a second Dewar containing liquid helium and the crystal was immersed directly into the helium bath. At the normal boiling point of liquid helium the boiling action perturbed the system and prevented accurate magnetic measurements. A temperature of 1.8°K was then obtained by pumping on the bath and at this temperature the superfluid character of the helium left the system unperturbed so that the magnetic measurements could be made.

In our previous publication[1] we indicated that the permanent moment could be increased with soft x irradiation. We have continued these measurements in a more intense beam (5 mA, 20 000 V) and we have again found that the magnitude of the permanent moment increases with soft x irradiation. We have also found that with continued x irradiation the permanent moment goes through a maximum and then sharply decreases, and with even longer exposures the permanent moment has been observed to vanish completely.

The intensity of the x-ray beam was determined using a $\frac{1}{32}$-in. by 1-in. NaI(Tl) crystal and a Hamner SX-10 low noise preamplifier designed for use in the soft x-ray range. An aluminum filter of thickness 2445 mg/cm^2 was used to reduce the intensity of the beam

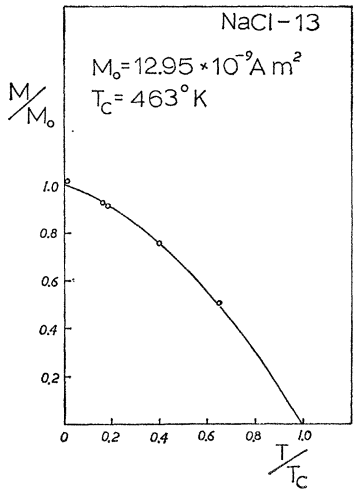

FIG. 3. The temperature dependence of the permanent magnetic moment for NaCl-13. The theoretical curve for spin waves in a ferromagnet is made to pass through the observed points in order to deduce a Curie temperature of 463°K. $M=M_0[1-(T/T_c)^{3/2}]$.

[3] The crystal had never been in a magnetic field and no absorption bands were found in the visible region.

[4] F. Bloch, Z. Physik **61**, 206 (1930).

TABLE I. The temperature dependence of the permanent moment (in 10^{-9} A m^2) for three different samples, NaCl-13, NaCl-7, and KCl-6. The values of the magnetic moment at absolute zero M_0 are given and the calculated Curie temperatures T_c are given.

	1.8°K	78°K	88°K	184°K	295°K	M_0	T_c
NaCl-13	13.20	11.94	11.74	9.73	6.73	12.95	463°K
NaCl-7	8.82	8.20	•••	•••	4.38	8.83	461.8°K
KCL-6	11.52	10.92	•••	•••	6.84	11.53	545.4°K

approximately 100 times and the resulting beam was used to irradiate our samples. The flux of the beam under these conditions was found to be 1.24×10^4 photons/cm^2 sec incident upon the surface of the samples. During the irradiation process the samples were continuously rotated in the beam to ensure that the entire surface of the crystal would receive uniform radiation damage.

The magnitude of the permanent moment was determined before x irradiation and immediately after each 30-sec exposure. Figure 4 shows the normalized magnitude of the permanent moment for NaCl-4 after each 30-sec exposure plotted against the total number of photons incident upon each cm^2 of sample. After 150 sec of exposure the permanent moment reached its maximum value of 2.70×10^{-9} Am^2, and with continued x irradiation the permanent moment dropped below its initial value prior to any x irradiation. After 270-sec exposure the value of the permanent moment was substantially lower than the preirradiation value

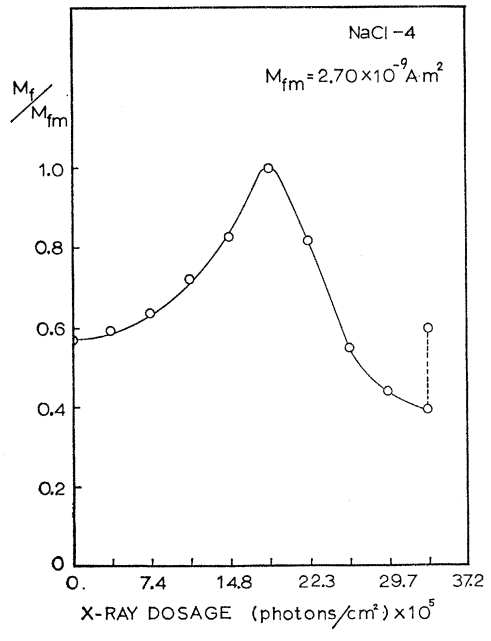

FIG. 4. The permanent magnetic moment versus the number of photons incident upon each cm^2 of sample. The abscissa is divided into 30-sec intervals and the maximum value of the permanent moment is given by $M_{fm}=2.70\times10^{-9}$ Am^2 for NaCl-4. The photon flux is 1.24×10^4 photons/cm^2 sec. The higher of the two points connected by the dashed line is the result of aging the sample for a period of one month after the lower of the two points had been obtained.

and if the exposure were continued for approximately 1800 sec longer the permanent moment would become unobservable. The higher of the two points connected by the dashed line in Fig. 4 was obtained after the crystal was aged for approximately one month. It is worth noting that the permanent moment returned to its preirradiation value after this one month of aging to within 1.3%.

Measurements of the permanent moment as a function of the number of incident photons have also been carried out on a sample of potassium chloride KCl-4 and similar results were obtained. The curve had the same general shape as did the one for NaCl-4 and after one month aging the permanent moment returned to its preirradiation value to within 7%.

CONCLUSIONS

The same Curie temperature to within 2°K has been obtained for two different samples of NaCl. These samples had different values of the magnetization at absolute zero: 12.95×10^{-9} Am^2 for NaCl-13 and 8.83×10^{-9} Am^2 for NaCl-7, which indicates that the Curie temperature is a property of the substance sodium chloride and not of the particular sample or the number of dislocations present in a given sample. This is even more significant in view of the fact that the Curie temperature of KCl was found to be 545°K.

It is not unreasonable to assume that there are 10^6 dislocation lines per cm^2 in these crystals. In fact special precautions must be taken to grow single crystals of the alkali halides with a dislocation density as low as 3×10^3 dislocations per square centimeter.[5] With 10^8 electrons per cm of dislocation line (since the interatomic distance is of the order of 10^{-8} cm) a value of 10^{14} electrons per cm^3 of salt would be expected. From the value of the magnetic moment measured for NaCl, $M_0=12.95\times10^{-9}$ Am^2, a value of 10^{14} electrons per cc has been obtained as follows: $M_0/V\mu_\beta=1.96\times10^{14}$, where $V=7.19$ cm^3 and μ_β is the Bohr magneton.

The experimental evidence showing first an increase in the magnitude of the permanent moment with soft x rays followed by a rapid decrease and vanishing of the permanent moment with longer exposure to x rays can be understood in the following manner. Electrons may be liberated by x rays from the valence band into the conduction band, and they may be trapped at dislocation lines to a depth of 0.24 eV for KCl.[6] In the

[5] E. Schonherr, Phys. Letters **20**, 241 (1960).

[6] H. Kawamura and H. Okura, J. Phys. Chem. Solids **8**, 161 (1959).

early stages of x irradiation there is a low density of trapped electrons, hence a ferromagnetic state exists. As the x-ray bombardment is continued the concentration of trapped electrons increases and there are very few unpaired electrons resulting in the destruction of the ferromagnetic state.

According to the theory of Bloch[7] the ferromagnetic state exists for low concentrations of electrons because the electrons have parallel spins and stay far apart in order to keep their Coulomb repulsion reduced as much as possible. This is a direct consequence of the Pauli exclusion principle.

It has also been observed that if the crystals are permitted to age approximately one month with respect to the last period of x irradiation, the magnetic moment returns the value it had prior to any x irradiation, indicating that the trapped electrons are only stable in a specified concentration per dislocation given by the preirradiation value. High concentrations may slowly evaporate away at room temperature if the trapping depth is small.

The experimental evidence presented in this paper would seem to rule out the possibility that the observed ferromagnetism arises from nickel or iron precipitates in the crystal. It does however support the idea that the ferromagnetic effect arises from the 10^{14} electrons trapped at dislocations in these crystals.

[7] F. Bloch, Z. Physik **57**, 545 (1929).

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Experimental Determination of the Optical Density of States in Iron*†

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Energy distributions of photoemitted electrons and the spectral distribution of quantum yield from iron ($\phi=4.8$ eV) have been measured to a maximum photon energy of 11.6 eV. These data are presented and interpreted in terms of the electronic structure of iron. No evidence is found in these data consistent with the assumption that conservation of **k** is an important selection rule. Rather, it is found that the data can be interpreted in a consistent manner if the optical transition probability is assumed to depend only on the initial and final densities of states. The results allow determination of the optical density of states in the regions $-6.0\leq(E-E_F)\leq 0$ and $5.5\leq(E-E_F)\leq 11.6$ eV, where E_F is the energy of the Fermi level. Maxima are found in the valence-band optical density of states at 0.35, 2.4, and 5.5 eV below E_F. This result is similar to that obtained in nickel, except the lowest-energy peak is not as strong and occurs at a lower energy in iron. The conduction-band optical density of states is approximately constant in the region observed. The iron samples were also coated with approximately one monolayer of cesium to reduce the work function ($\phi=1.55$ eV) and thereby extend the range of measurements. Strong transitions are observed near $\hbar\omega=2$ eV, for which the matrix elements vary markedly with $\hbar\omega$. The results, obtained at higher photon energies, are in reasonable agreement with the noncesiated data and suggest that the conduction-band optical density of states decreases monotonically by a factor of two between 2.5 and 5 eV above E_F.

I. INTRODUCTION

IN an earlier paper,[1] the photoemission data on nickel were presented and analyzed. It was shown that the optical density of states[2,3] of Ni obtained from these data differs markedly from that of Cu and that the two are not simply related via the rigid-band model. In this paper, photoemission studies on iron are reported. Iron was chosen as the second ferromagnetic metal to study because the experimental data from Fe coupled with that from Ni would span the three common ferromagnetic metals—Fe, Co, and Ni. A comparison of the experimentally determined electronic structures of Fe and Ni is of particular interest because of the various theoretical models which have been advanced concerning the electronic structure and ferromagnetism in these two metals.[4]

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† Based on a thesis submitted by A. J. Blodgett, Jr., IBM Resident Fellow, to Stanford University in partial fulfillment of the requirements of the Ph.D. degree.

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[1] A. J. Blodgett, Jr., and W. E. Spicer, Phys. Rev. **146**, 390 (1966).

[2] The densities of state obtained from photoemission and optical measurements are called optical densities of states. See Ref. 3.

[3] W. E. Spicer, Phys. Rev. **154**, 385 (1967).

[4] See, for example, N. Mott, Advan. Phys. **13**, 325 (1964), and references given therein.