CHLORINE NUCLEAR MAGNETIC RESONANCE IN PARAMAGNETIC AND ANTIFERROMAGNETIC $FeCl_2$

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(Received 18 September 1964)

The combined nuclear quadrupole-nuclear magnetic (NQNM) interaction has been investigated for chlorine nuclei in the paramagnetic and antiferromagnetic states of single-crystalline $FeCl_2$. The present results agree with the previous room-temperature results.[1,2] The analysis of the resonance patterns is simplified by crystalline and magnetic symmetry, unlike recently reported examples.[3,4]

In the paramagnetic region, a Varian wide-line spectrometer with associated magnet was used to detect the Cl^{35} magnetic resonances. In the antiferromagnetic state, a super-regenerative spectrometer with sinusoidal magnetic modulation and double frequency detection was used. A single-crystal specimen of size $3\times4\times5$ mm^3 was used and mounted such that it was possible to bring the crystalline c axis into directions coaxial and perpendicular to the applied magnetic field.

The NQNM Hamiltonian has been given by Pound[5] and Matthias, Schneider, and Steffen,[6] among others. When effects due to isotropic and anisotropic paramagnetic shifts, K_{iso} and K_{ax}, respectively, are included in the Hamiltonian, extraction of the pertinent parameters from the high-frequency satellite transitions is given by

$$\nu_{obs}(\theta=0^\circ)=\nu_R(1+K_{iso}+2K_{ax})+\nu_Q, \qquad (1)$$

$$\nu_{obs}(\theta=90^\circ)=\nu+\nabla_+-\nabla_-, \qquad (2)$$

where $\nabla_\pm=[\nu^2\pm\frac{1}{2}\nu\nu_Q+\frac{1}{4}\nu_Q{}^2]^{1/2}$, $\nu=\nu_R(1+K_{iso}-K_{ax})$, $\nu_Q=e^2q(Cl)Q(Cl)/2h$, $\nu_R=\gamma(Cl)H/2\pi$, and θ is the angle between the direction of the applied magnetic field and the crystalline c axis. Equation (2) can be solved graphically and reduces for the present case to

$$\nu(\theta=90^\circ)=\nu_R(1+K_{iso}-K_{ax})=6.828 \text{ Mc/sec}, \qquad (2')$$

the constant being derived from the evaluation of ν_Q and the frequency of the resonance condition (in our case fixed at 8 Mc/sec). For the orientation $\theta=0^\circ$, a plot of the nuclear magnetic-resonance frequency versus the magnetic field (at constant temperature) extrapolated to zero field yields, for Eq. (1), the value of the quadrupole-interaction frequency, ν_Q. This was done for the temperatures 77°K, 160°K, and 303°K, and the value of ν_Q was 2.37 ± 0.01 Mc/sec for all three temperatures. As a result of the temperature independence of ν_Q, determining the magnetic field necessary for the resonance condition (which evaluates ν_R) at constant frequency and constant temperature for the angles $\theta=0^\circ$ and 90° yields, via Eqs. (1) and (2'), the shift parameters. This was done at 10 different temperatures and the results obtained for K_{iso} and K_{ax} are plotted as a function of $1/(T-23.6^\circ\text{K})$ in Fiq. 1. A plot of the reciprocal bulk shift in the $\theta=0^\circ$ orientation versus the absolute temperature yields a temperature intercept of 30°K.

Below the ordering temperature, a three-resonance pattern was observed for both the Cl^{35} and Cl^{37} isotopes with a frequency separation indicating a value of ν_Q identical to that in the paramagnetic state. The frequencies of the resonances correspond to an effective magnetic field at the chlorine nuclear sites of 77 kOe at 4.2°K. The resonances were observable with maximum intensity when the magnetic modula-

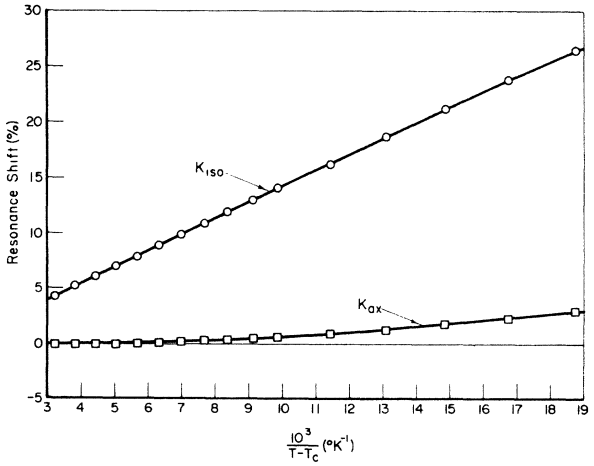

FIG. 1. K_{iso} and K_{ax} as a function of $1/(T-T_c)$, where $T_c=23.6$°K.

tion was directed along the c axis and unobservable when directed perpendicular to the c axis. This fact, together with the value of the quadrupolar splitting, indicates that the effective field is directed along the c axis.

The resonances in the antiferromagnetic state were observed as a function of temperature in the ranges 2-4°K and 14-15.5°K and the data are plotted in Fig. 2. As the temperature approached 15.5°K the resonances, already at least 50 kc/sec wide at 4.2°K, decreased in intensity and disappeared, presumably due to broadening. Upon application of an external magnetic field directed along the c axis at 4.2°K, each resonance split into two resonances corresponding to $H_{\text{eff}} = H_{\text{int}} \pm H_{\text{ext}}$, similar to the pattern obtained by Jaccarino[7] in CoF_2. The plot of frequency versus H_{ext} yielded straight lines of slope equal to ±0.417 Mc/sec-kOe, the value of the gyromagnetic ratio for the free chlorine ion. The resonances were observable in external fields up to 10.5 kOe, but were unobservable in fields from 11 to 18 kOe. This disappearance is attributed to spin flipping of layers of ion moments and lack of sufficient magnetic order.

$FeCl_2$ crystallizes[8] in the $CdCl_2$ structure ($D_{3d}^5 - R\bar{3}m$), and Barnes and Segel[1] have demonstrated that the principal axis of the electric field gradient is directed along the c axis and effects of anisotropy in the gradient are absent. Barnes et al.[9] have also shown that the contribution to the quadrupole coupling from the ion-lattice background is small compared to the experimental value, the implication being that the major contribution comes from covalent bonding. Further evidence for covalent bonding is afforded by the magnitude of the paramagnetic shifts as well as the large value of the hyperfine field at the chlorine nuclear sites in the antiferromagnetic state. Yomosa[10] has estimated the dipole field to be only of the order of 10 kOe. Wilkinson et al.[11] have demonstrated by means of neutron diffraction that the iron-ion moments lie normal to the basal plane, from which one would expect the dipole field to be directed along the c axis. Our experiments indicate that the effective magnetic field at the chlorine sites is indeed in that direction.

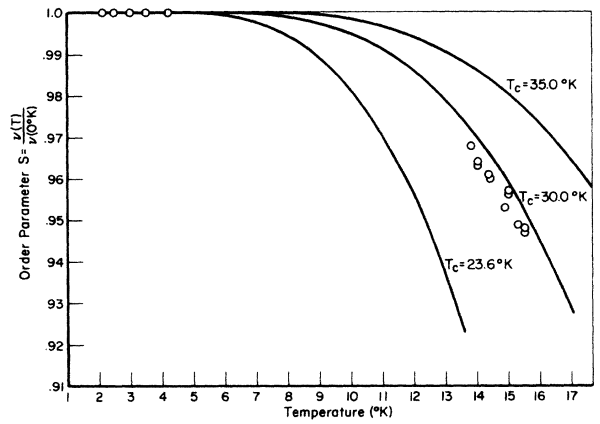

FIG. 2. Order parameter as a function of temperature. s is obtained by evaluating the ratio (resonance frequency at given temperature)/(resonance frequency at 2°K). The curves are plots of the function $\ln(1+s)/(1-s) = 13.2As/kT$ for three values of T_c, where $A/k = 0.153\,T_c$.

Various authors[12,13] have established that the ordering temperature in $FeCl_2$ is 23.6°K and not the 30°K that we have determined from the bulk shift. Our data seem to be characterized by the latter temperature. The curves in Fig. 2 are plots of the function $\ln(1+s)/(1-s) = 13.2As/kT$, where A is determined from $T_c = A/0.153k$ and s is the order parameter. These equations are given by Yomosa as the result of a molecular-field approximation. The curves for T_c equal to 23.6°K, 30°K, and 35°K are given. We feel that the choice of an ordering temperature of about 30°K to fit the data both above and below the transition is somewhat fortuitous, and indeed Domb[14] has pointed out that extrapolation of experimental data far removed from the ordering temperature tends to yield values of the ordering temperature which are too high.

Further experiments are under way to determine the spin-flip field, details of the sublattice magnetization below the ordering temperature, and values of the shift parameters above the ordering temperature.

The authors express their thanks to Dr. J. W. Stout for loan of single-crystal specimens and for valuable discussions, and one of us (S. L. S.) wishes to thank the Battelle Memorial Institute for its hospitality during the performance of experiments.

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ANISOTROPIC ENERGY LOSS OF LIGHT PARTICLES OF MeV ENERGIES IN THIN SILICON SINGLE CRYSTALS*

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(Received 17 September 1964)

Recent experiments[1,2] show that the ionization loss of a beam of fast light particles passing through a thin Si single crystal is strongly dependent on orientation. When the beam enters the crystal along one of the low-index crystal axes, the energy spectrum of the transmitted particles differs markedly from a Gaussian distribution and has a broad "shoulder" towards the high energies. Dearnaley[1] suggests that this effect is due to the correlated small-angle collisions between the penetrating particles and the lattice atoms. As a result of such collisions the particles are deflected away from the vicinity of nuclei (hence from regions of high electron density) and "channeled" along the crystal axes where the electron density is low. Such a mechanism was previously proposed by Nelson and Thompson[3] to account for the enhanced transmission of 75-keV protons in thin Au foils. No quantitative treatment of the degree of anisotropy to be expected from "channeling" has been given so far. The purpose of this Letter is to report new experimental evidence indicating that (i) the anisotropy of energy loss is characteristic of the low-index symmetry planes of the crystal and shows up strongly along crystal axes where such planes intersect, (ii) the fraction of the transmitted beam with energies in the "tail" or "shoulder" of the distorted spectrum is relatively insensitive to the collimation of the incident beam, and (iii) in addition to the distortion towards high energies there is also an increase in the energy straggling at the low-energy end of the spectrum.

An explanation based on correlated small-angle deflections is supported by very recent observations[4] on the dependence of macroscopic nuclear cross sections of (p,n) and (p,γ) reactions on orientation. Our evidence on energy loss favors the hypothesis that for fast light particles a mechanism of correlated deflections from atoms lying in low-index symmetry planes is essential to the phenomenon, rather than that of channeling along low-index atom rows. This latter process was predicted by machine calculations[5] and appears to be operative in the case of heavy ions of keV energies.[6,7] Some evidence for "interplanar channeling" with light ions near 50 keV in Cu and Au was obtained by Nelson and Thompson[3] from reflection data. More theoretical work is needed to clarify both processes.

A beam of 3-MeV protons (stable to ±1 keV) from the Brookhaven Van de Graaf accelerator was scattered elastically from a target of gold and collimated within a half-angle of divergence of about 0.05° on a 1-mil thick single crystal of silicon cut normal to the ⟨111⟩ axes. The crystal was prepared as a diffused-junction particle detector, using phosphorus diffusion and planar etching techniques described elsewhere.[2] A goniometer allows the adjustment of the angle of the plane of the crystal with respect to the beam direction and also the rotation of the crystal in its plane. The angular adjustments in the system were reproducible to ±0.1° by direct read-out of vernier scales and the accuracy of the goniom-