Internal Field Studies of Ferromagnetic CrI_3 by Means of the Mössbauer Effect in I^{129}

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The Mössbauer effect in the 27.8-keV transition of I^{129} was used to measure the coupling constants of the internal fields of the insulating ferromagnet CrI_3 above and below the Curie temperature (T_C). Above T_C, at 78°K, the following parameters were obtained: $e^2qQ(I^{127}) = +662\pm8$ Mc/sec; $\eta = 0.35\pm0.05$; isomer shift $= +0.23\pm0.05$ mm/sec with respect to a $Zn^{66}Te^{129}$ ($T_{1/2}=70$ m) source at 80°K. Below T_C, at 21°K, we deduce the following: $H_i = 25\pm5$ kOe; $\cos\beta = 0.45\pm0.05$. The e^2qQ value at 21°K was 727 Mc/sec, 10% greater than that at 78°K.

EXTENSIVE studies have been conducted on the magnetic properties of the insulating magnetic crystals of chromium trihalides. Internal fields were measured by NMR both in Cr^{53}—in all the trihalides[1]—and in Br^{79} and Br^{81} in $CrBr_3$.[2]

Mössbauer effect (ME) measurements in $CrI_3{}^{127}$ were carried out by Kalvius *et al.*[3] However, because of the intrinsic broad linewidth of the I^{127} level ($E_\gamma = 57.6$ keV) as compared with the coupling constants of the internal fields produced at the iodine nucleus, no splitting could be observed. Nevertheless, from the broadening of the absorption line above and below the Curie point, a relation between the quadrupole coupling and the magnetic field was deduced. Since this method involves considerable uncertainties we have remeasured the coupling constants in CrI_3 using the ME in the 27.8-keV level of I^{129}, which by virtue of its spectroscopic properties [$\Gamma(127)/\Gamma(129) = 9$] gives more accurate results.

The detailed structure of CrI_3 is still uncertain, but there is strong evidence that it is identical to $CrBr_3$[4] or differs at most in the stacking arrangement. The Curie temperature, as measured by Hansen and Griffel,[5] is $T_C = 70$°K.

Polycrystalline $CrI_3{}^{129}$ was prepared by heating stoichiometric proportions of chromium and molecular iodine at 500°C for seven days. Any excess of nonreacted iodine was then removed. The absorber (17 mg/cm² of I^{129}) was prepared by mixing the powdered sample with glass powder. The absorber temperatures (78 and 21°K) were attained by attaching the absorber to a commercial cryostat "CRYO-TIP,"[6] which operates from liquid-hydrogen up to liquid-nitrogen temperature. The source used was $Zn^{66}Te^{129}$ ($T_{1/2}=70$ m), and it was held at 80°K. The ME spectrometer was of the constant-acceleration type, incorporating a 1001 CN TMC multichannel analyzer operating in the multiscaler mode.

The quadrupole splitting spectrum above the Curie temperature is shown in Fig. 1(a). The spectrum is composed of eight lines corresponding to nuclear transitions between the excited state ($I^*=\frac{5}{2}$) and the ground state ($I=\frac{7}{2}$) of I^{129}. The line positions are given by the following expression[7]:

$$E_{ij} = e^2qQ_g/4\,[Rf(I^*, m_j^*, \eta) - f(I, m_i, \eta)] + \delta, \quad (1)$$

where e^2qQ_g is the quadrupole coupling constant, η is the asymmetry parameter of the electric field gradient (efg) tensor, $R = Q_{ex}/Q_g$ ($=1.231$),[8] δ is the isomer shift, and $f(I, m, \eta)$ is related to the spin Hamiltonian eigenvalues. The values of $f(I, m, \eta)$ (taken from Cohen's[9] compilation) were chosen so as to obtain the best fit with the experimental results. The following parameters were found:

$$e^2qQ(I^{127}) = +662\pm8 \text{ Mc/sec},$$
$$\eta = 0.35\pm0.05,$$
$$\delta = +0.23\pm0.05 \text{ mm/sec},$$

where e^2qQ is given in terms of the I^{127} quadrupole moment. This value of e^2qQ is considerably higher than the 560 Mc/sec reported by Kalvius *et al.*[3] No NQR experimental results have been published. The number of "unbalanced" p electrons U_p[10] was calculated from the quadrupole coupling constant and found to be

$$U_p = -(e^2qQ/e^2q_{at}Q) = 0.28, \quad (2)$$

which is higher than the value 0.13 deduced from the e^2qQ of Br in $CrBr_3$.[2] Since the η value is almost the same as that in $CrBr_3$ ($\eta=0.29$), which points to a similar Cr-halogen-Cr angle,[11] the higher value of U_p in the case of CrI_3 suggests that the Cr–I bond is more covalent than the Cr–Br bond. Since $Q(I^{127})$ is negative, the positive sign of e^2qQ shows[9] that the bonding is chiefly by the p_x and p_y electrons, i.e., the principal axis of the efg (q_{zz}) is perpendicular to the Cr–I–Cr plane, which is consistent with the atomic arrangement.

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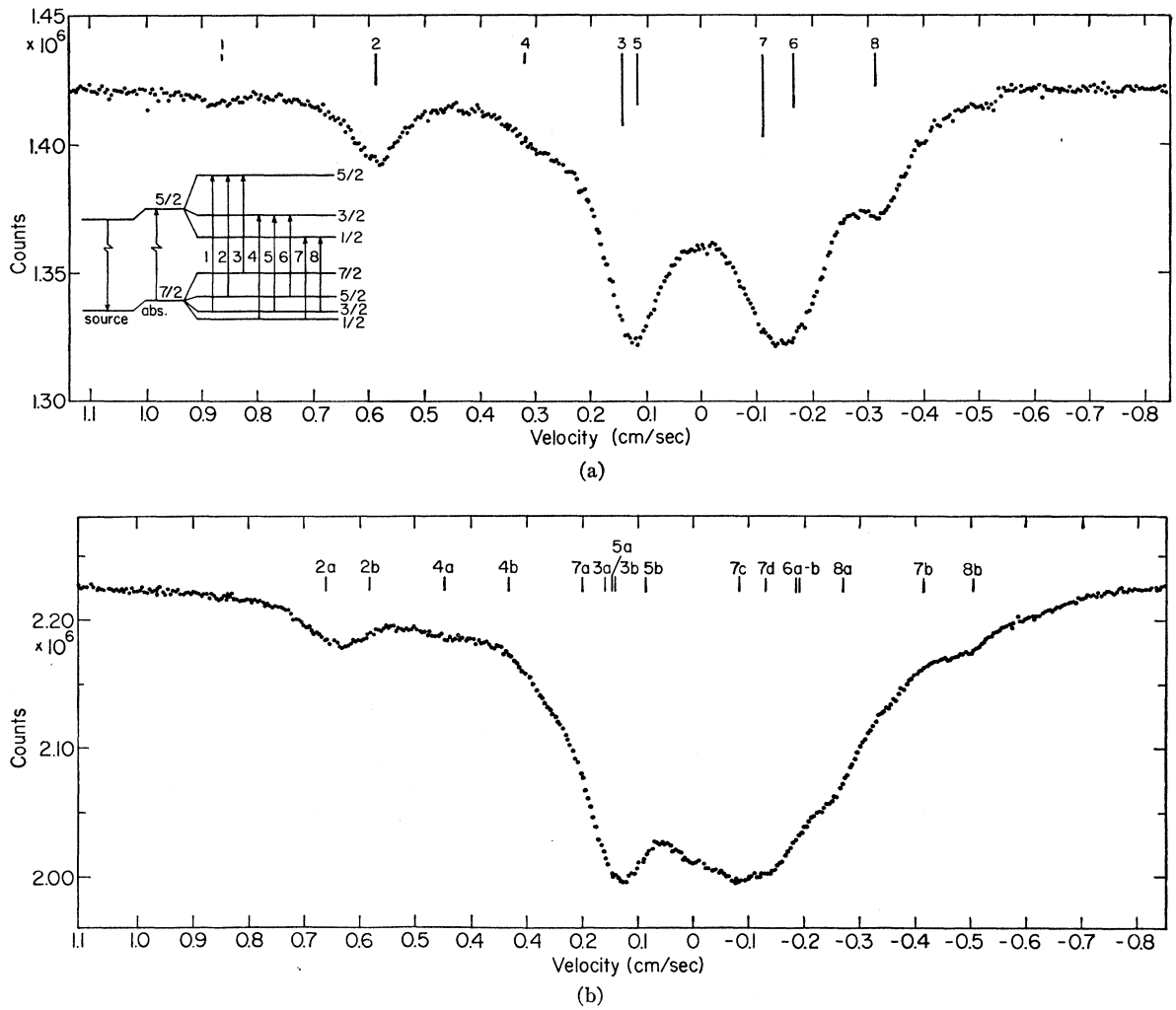

FIG. 1. (a) The quadrupole splitting spectrum of CrI_3^{129} at 78°K. (b) The spectrum of CrI_3^{129} at 21°K. The numbers refer to the transitions shown in (a). Subscripts a and b correspond to transitions $-m\rightarrow-m'$ and $+m\rightarrow+m'$ respectively. 7_c and 7_d correspond to transitions $-\frac{1}{2}\rightarrow+\frac{1}{2}$ and $\frac{1}{2}\rightarrow-\frac{1}{2}$, respectively.

The spectrum of CrI_3^{129} below the Curie temperature is shown in Fig. 1(b). The main differences between this spectrum and that found for the pure quadrupole interaction [Fig. 1(a)] are (a) Transition 1 is not detected, (b) the peak corresponding to transition 2 has become broad, and (c) the central peaks 3, 5, 6, 7, and 8 have merged into a broad peak which is hardly resolved.

In order to extract the internal field coupling we used the computer program developed by Gabriel and Ruby[12] to compute the eigenvalues corresponding to spin $\frac{5}{2}$ and $\frac{7}{2}$, as well as the transition energies. Unfortunately, we had trouble using the program on our computer to calculate the intensities, and therefore no intensities are given in Fig. 1(b).

The energy positions of the 18 allowed transitions between the six excited and eight ground levels are functions of the following unknown parameters: (a) the quadrupole coupling constant e^2qQ, (b) the asymmetry parameter η, (c) the intensity of the iodine internal field H_i, and (d) the angle β between the direction of q_{zz} and H_i. We calculated the energy positions for a wide range of the parameters a, c, and d using the values $\mu_{ex}=2.84$, $\mu_{Gd}=2.617$,[13] $R=1.231$, and $\eta=0.35$. Since in our case $\eta\neq0$, there may be additional transitions due to mixing of the m states. We have neglected these transitions, assuming that their intensities (for $\eta=0.35$) will be small.

The energy positions of transitions $2(-\frac{5}{2}\rightarrow-\frac{5}{2}$ and $\frac{5}{2}\rightarrow\frac{5}{2})$ and $8(-\frac{1}{2}\rightarrow-\frac{3}{2}$ and $\frac{1}{2}\rightarrow\frac{3}{2})$ as a function of H_i for $e^2qQ=713$ Mc/sec and different values of $\cos\beta$, are shown in Fig. 2.

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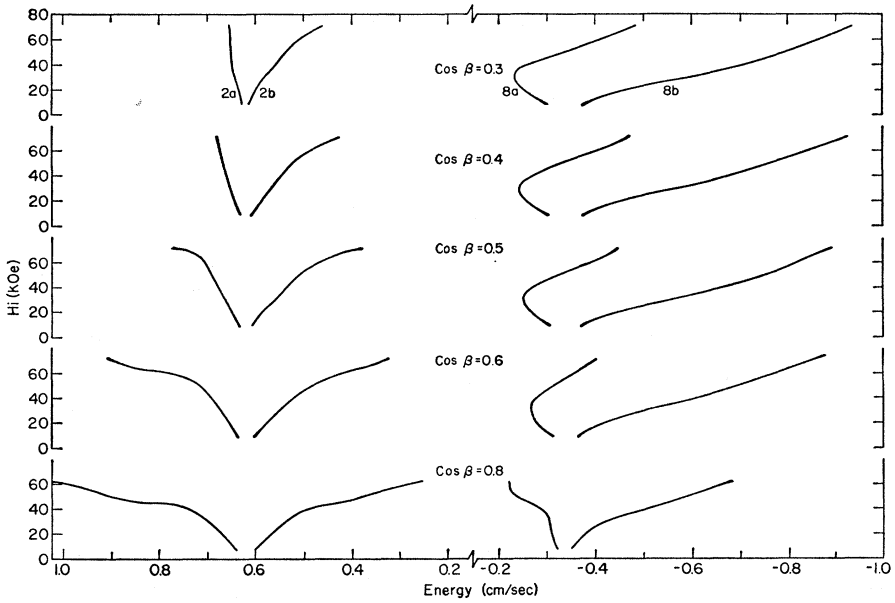

FIG. 2. The positions of transitions 2 and 8 as a function of H_i for $e^2qQ=713$ Mc/sec and different values of $\cos\beta$.

From the calculated line positions and the spectrum shown in Fig. 1(b) we note the following:

(a) The centroid of transition 2 in Fig. 1(b) has shifted towards a higher energy as compared with its position in Fig. 1(a). This cannot be explained by the general behavior of the centroid of this transition under the influence of H_i and $\cos\beta$. In fact, any change in these two parameters tends to shift it towards lower energy (Fig. 2). Neither can an increase in η account for the observed phenomenon, since the influence of η on the position of line 2 is very small.[7] Therefore the experimental result can only be due to a larger value of e^2qQ below the Curie temperature. Assuming that the isomer shift does not change on crossing T_C (the second-order Doppler shift is negligible) we found that e^2qQ (below T_C) $=727$ Mc/sec, which is approximately 10% greater than above T_C, and indicates an increase in covalency.

(b) The nondetection of transition 1 after its magnetic splitting is to be expected, in view of the weakness of this transition.

(c) Transition 7 splits into four lines and the magnitude of the splitting is appreciable even at low values of H_i.

(d) Transitions 3 and 5 are slightly affected by H_i and $\cos\beta$. Points (c) and (d) explain the shape of the central part of the spectrum.

(e) From Fig. 2 we note that the centroid of transition 8 is markedly shifted outwards, the higher the value of H_i and the lower the value of $\cos\beta$. Also, the splitting of transition 2 increases with increasing values of H_i and $\cos\beta$.

The experimentally observed broadening of transition 2 corresponds to $H_i=32$ kOe if $\cos\beta=0.3$ and to $H_i=14$ kOe, if $\cos\beta=0.8$. In the first case the position of 8b would be expected to be at a lower energy than in Fig. 1(b), and in the second case at a higher energy.

The best fit of the observed broadening and the positions of 8b and 2 gives the following values:

$$H_i=25\pm5\text{ kOe},$$
$$\cos\beta=0.45\pm0.05,$$
$$e^2qQ=727\pm10\text{ Mc/sec}.$$

In Fig. 1(b) the position of the transitions calculated with the above values are indicated.

The value of H_i is markedly less than that computed by Kalvius *et al.*, who found the value of $H_i=140\pm30$ kOe from the broadening of the linewidth below the Curie temperature. It should be noted that the latter value was calculated assuming that e^2qQ is the same below as above the Curie temperature.

The values of H_i and $\cos\beta$ are less than those found for Br in $CrBr_3$ ($H_i=37.7$ kOe and $\cos\beta=0.67$ at 0°K).

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