

# Mössbauer Study of Metamagnetic Transition in FeCl<sub>2</sub> and FeBr<sub>2</sub>†

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The metamagnetic (spin-flop) transition is studied in single crystals of FeCl<sub>2</sub> and FeBr<sub>2</sub> using the Mössbauer effect and external magnetic fields up to 40 kG. From the changes which take place in the  $m = \frac{1}{2} \rightarrow m^* = \frac{3}{2}$  and  $m = -\frac{1}{2} \rightarrow m^* = -\frac{3}{2}$  transitions when FeBr<sub>2</sub> passes through the spin-flop, the sign of the internal field at the nucleus is found to be positive. In addition, the difference between the interionic dipolar fields above and below the spin-flop transition is determined as  $-6.7$  kG for FeBr<sub>2</sub>. The interionic dipolar fields are also calculated for FeCl<sub>2</sub>, FeBr<sub>2</sub>, and FeI<sub>2</sub> above and below the spin-flop. The calculated difference for FeBr<sub>2</sub> is  $-6.8$  kG, in good agreement with the experimental difference. The internal magnetic field at the iron nucleus in FeCl<sub>2</sub> is found to be  $-5.0$  kG above the spin-flop. This result is used with the calculated lattice sums to determine the internal field below the spin-flop. A value of  $+2.8$  kG is found for this field, in agreement with earlier observations. The sign of the internal field in FeI<sub>2</sub> is predicted to be positive. Increasingly positive internal fields going down the series FeCl<sub>2</sub>, FeBr<sub>2</sub>, and FeI<sub>2</sub> are consistent with the interpretation that the iron-halogen bond is increasingly covalent. This is manifested in an increasing fraction of  $4s$  electron character in the Fe<sup>2+</sup> electronic configuration.

## I. INTRODUCTION

**A**NHYDROUS ferrous chloride and ferrous bromide are both low-temperature antiferromagnets exhibiting the spin-flop phenomenon (metamagnetism).<sup>1,2</sup> Their unusual magnetic properties have been studied with a variety of techniques, including the Mössbauer effect,<sup>3,4</sup> and have also been treated theoretically.<sup>5,6</sup> In spite of the wealth of literature dealing with these and similar materials, a full understanding of the internal magnetic field at the nucleus has not yet been attained. It seemed that valuable additional information could be obtained by observing the effects of an external magnetic field on the Mössbauer spectrum. In this way the sign of the internal field may be established and the effects of the spin-flop transition on the field at the iron nucleus determined.

FeCl<sub>2</sub> has the CdCl<sub>2</sub> structure and FeBr<sub>2</sub> the CdI<sub>2</sub> structure.<sup>7</sup> Both materials have their spins aligned antiparallel along the threefold axis below their respective Néel temperatures (24°K for FeCl<sub>2</sub> and 11°K for FeBr<sub>2</sub>).<sup>1,2</sup> Upon application of a sufficiently large external field (10.5 kG for FeCl<sub>2</sub> and 31.5 kG for FeBr<sub>2</sub>) in the direction of the spins, the antiparallel sublattice flops and the crystals become ferromagnetic.

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<sup>1</sup> C. Starr, F. Bitter, and A. R. Kaufmann, *Phys. Rev.* **58**, 977 (1940).

<sup>2</sup> W. C. Koehler and E. O. Wollan, *Bull. Am. Phys. Soc.* **1**, 190 (1956).

<sup>3</sup> K. Ôno, A. Ito, and T. Fujita, *J. Phys. Soc. Japan* **19**, 2119 (1964).

<sup>4</sup> Elmar Pfletschinger, *Z. Physik* **209**, 119 (1968).

<sup>5</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **20**, 890 (1958).

<sup>6</sup> A. Okiji and J. Kanamori, *J. Phys. Soc. Japan* **19**, 908 (1964).

<sup>7</sup> Ralph W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience, Inc., New York, 1965), 2nd ed., Vol. 1.

## II. EXPERIMENTAL PROCEDURE AND RESULTS

### A. Sample Preparation

FeBr<sub>2</sub>·4H<sub>2</sub>O was prepared by dissolving iron metal in HBr. The product was dehydrated at 400–500°C in HBr gas. Crystals were then grown from the melt by the standard Bridgman technique. The single crystals of FeCl<sub>2</sub> used were prepared by Trapp.<sup>8</sup>

Thin sheets were carefully peeled from the crystals and mounted in protective Lucite holders. The Lucite holders were then mounted in the helium bore of a Westinghouse superconducting solenoid. The actual sample temperatures were not measured, but other experiments with the solenoid used under similar conditions gave sample temperatures of about 5°K. The crystals were oriented with the trigonal axis along the field direction, which was also the direction of propagation of the  $\gamma$  rays.

### B. Mössbauer Spectrometer

The Mössbauer spectrometer used employed a constant acceleration electromechanical drive. Data were stored in a 400-channel analyzer operating in the time mode. A 20-mCi Co<sup>57</sup> in Pd source was used throughout.<sup>9</sup> At zero applied field the experimental linewidths at half-height were 0.28 mm/sec for the  $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$  transitions in FeBr<sub>2</sub> and 0.35 mm/sec for the  $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$  transition in FeCl<sub>2</sub>.

### C. Procedure and Results

The spectrum was first measured at zero applied field. The field was then increased to the maximum ( $\sim 40$  kG) and succeeding measurements were made going down in field. The observed spectra are shown in

<sup>8</sup> C. Trapp, Ph.D. thesis, University of Chicago, 1962 (unpublished).

<sup>9</sup> B. J. Evans and S. S. Hafner, *J. Phys. Chem. Solids* (to be published).

Figs. 1 and 2. Although the zero-field spectra have been previously reported<sup>3,4</sup> they are included here for comparison. The quadrupole coupling constants, isomer shifts (relative to a  $\text{Co}^{57}$  in Pd source), and effective internal fields are listed in Table I. It should be noted that the absence of the  $\Delta m=0$  lines which results from the orientation of the single-crystal absorber reduces the number of unresolved lines, and in the case of  $\text{FeBr}_2$  permits one to deduce the internal field and quadrupole interaction without resorting to curve fitting.

Marked changes occur in the  $\text{FeBr}_2$  spectrum upon passage through the spin-flop transition. Below the flop field, when the spin arrangement is antiferromagnetic, the applied field is parallel to one sublattice and antiparallel to the other. Hence the effective field is increased for ions on one sublattice and correspondingly decreased for those on the other. This sublattice splitting collapses at the flop field. Higher fields simply increase

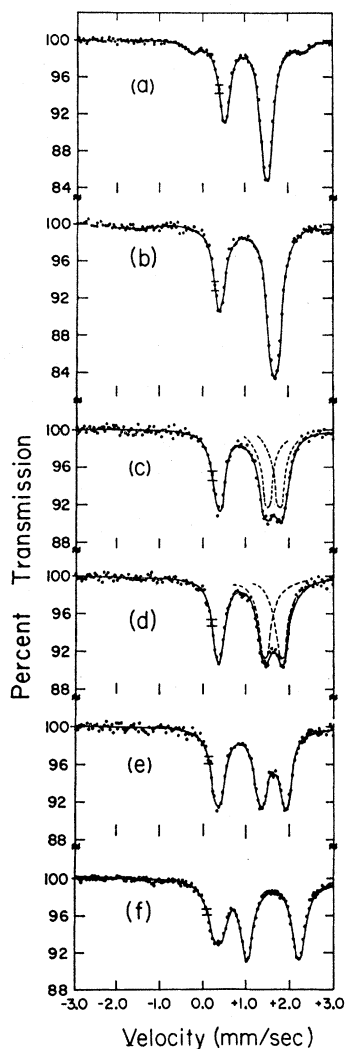


FIG. 1. Mössbauer spectrum of  $\text{FeCl}_2$  single crystal at various applied magnetic fields. (a)  $H_a=0$ , (b)  $H_a=8.48$  kG, (c)  $H_a=10.6$  kG, (d)  $H_a=14.9$  kG, (e)  $H_a=21.2$  kG, (f)  $H_a=39.0$  kG.

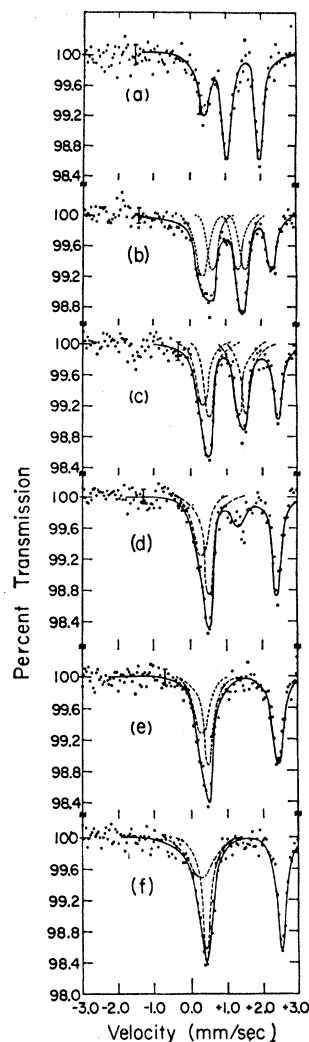


FIG. 2. Mössbauer spectrum of  $\text{FeBr}_2$  single crystal at various applied magnetic fields. (a)  $H_a=0$ , (b)  $H_a=21.2$  kG—lines, as labeled in Fig. 3, from right to left:  $E_2^A$ ,  $E_2^B$ ,  $E_1^B$ ,  $E_1^A$ . (c)  $H_a=29.65$  kG—lines, as labeled in Fig. 3, from right to left:  $E_2^A$ ,  $E_1^B$ ,  $E_2^B$ ,  $E_1^A$ . (d)  $H_a=32.85$  kG, (e)  $H_a=36.0$  kG, (f)  $H_a=39.0$  kG.

the effective field at the nucleus, and hence the over-all splitting. In the case of  $\text{FeCl}_2$  the flop field and the internal field are so small that sublattice splittings cannot be resolved, so that the spin-flop transition is not useful in determining the sign of the internal field. The changes which take place are illustrated in Figs. 3 and 4. Here the energies (in channel number) of the  $m=\frac{1}{2} \rightarrow m^*=\frac{3}{2}$  and  $m=-\frac{1}{2} \rightarrow m^*=-\frac{3}{2}$  peaks are plotted as a function of the applied magnetic field. These peaks were assigned on the basis of their intensities and the size of their splitting in the external field. They are the high-energy lines (high velocity) in both  $\text{FeBr}_2$  and  $\text{FeCl}_2$ , which indicates that the sign of the electric field gradient is positive ( $q_z > 0$ ), as previously reported by Öno<sup>3</sup> for  $\text{FeCl}_2$ .

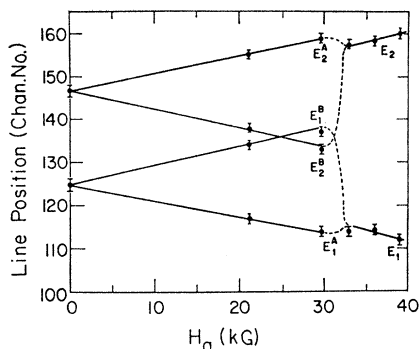


FIG. 3. Position of high-energy lines (high velocity) in  $\text{FeBr}_2$  at various applied magnetic fields. (Higher channel numbers correspond to higher velocities.) The solid lines are calculated line positions. Dashed lines indicate the collapse of the B sublattice line positions onto the A sublattice line positions.

The internal field at the iron nucleus can be written<sup>10,11</sup>

$$H_i = H_c + H_{\text{orb}} + H_{\text{dip}} + H_{\text{dip}}', \quad (1)$$

where  $H_c = a(|\psi\downarrow(0)|^2 - |\psi\uparrow(0)|^2)$  is the Fermi contact or core-polarization term,  $H_{\text{orb}} = 2\mu_B \langle r^{-3} \rangle \langle L_z \rangle$  is the orbital-current term,  $H_{\text{dip}} = \frac{1}{2}\mu_B q_z \langle S_z \rangle$  is the intraionic dipolar interaction term,<sup>5</sup> and  $H_{\text{dip}}'$  is the interionic dipolar field.  $\langle S_z \rangle$  and  $\langle L_z \rangle$  are components of spin and orbital angular momenta, in units of  $\hbar$ ,  $\mu_B$  is the Bohr magneton, and  $q_z$  is the electric field gradient at the nucleus [ $q_z = \langle r^{-3} \rangle \langle (3z^2/r^2) - 1 \rangle$ ]. Both  $H_{\text{orb}}$  and  $H_{\text{dip}}$  are positive (in the same direction as the ionic magnetic moment), while  $H_c$  is negative<sup>11</sup>;  $H_{\text{dip}}'$  must be determined by performing a lattice sum. The sign of  $H_i$  depends primarily on the relative magnitudes of  $H_c$  and  $H_{\text{orb}}$  because the dipolar terms are expected to be

TABLE I. Effective field, quadrupole splitting, and isomer shift (relative to  $\text{Co}^{57}/\text{Pd}$ ) at various applied fields.

	Applied magnetic field $H_a$ (kG)	Observed magnetic field $H_{\text{eff}}$ (kG)	Quadrupole splitting $\Delta E$ (mm/sec)	Isomer shift $\delta$ (mm/sec)
$\text{FeCl}_2$	0	0	$+0.98 \pm 0.02^a$	$+0.97 \pm 0.02$
	8.48	0	$+1.22 \pm 0.02^a$	$+0.97 \pm 0.02$
	10.6	8.1	$+1.29 \pm 0.02$	$+0.97 \pm 0.02$
	21.2	17.49	$+1.29 \pm 0.02$	$+0.97 \pm 0.02$
	39.0	37.7	$+1.29 \pm 0.02$	$+0.97 \pm 0.02$
$\text{FeBr}_2$	0	29.6	$+1.09 \pm 0.02$	$+0.94 \pm 0.02$
	21.2		$+1.09 \pm 0.02$	$+0.94 \pm 0.02$
	29.65		$+1.09 \pm 0.02$	$+0.94 \pm 0.02$
	32.85	57.86	$+1.09 \pm 0.02$	$+0.94 \pm 0.02$
	36.0	58.54	$+1.09 \pm 0.02$	$+0.94 \pm 0.02$
	39.0	64.59	$+1.09 \pm 0.02$	$+0.94 \pm 0.02$

<sup>a</sup> The quadrupole interaction was observed to increase in  $\text{FeCl}_2$  after the crystal was subjected to large external magnetic fields; the second measurement was made in zero field, after the crystal had been subjected to a field of 40 kG. No explanation can be offered for this phenomenon at the present.

<sup>10</sup> R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

<sup>11</sup> R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).

TABLE II. Calculated dipole fields. The lattice constants used were those given in Wyckoff (Ref. 7).

	$H_{A-B}$ (G) Antiferromagnetic	$H_{A+B}$ (G) Ferromagnetic
$\text{FeCl}_2$	-10 554	-2695
$\text{FeBr}_2$	-9416	-2572
$\text{FeI}_2$	-7610	-2280

small. Since covalency effects can influence either or both of these, a knowledge of the sign of  $H_i$  as well as its magnitude is useful in understanding the nature of the bonding in a given series of  $\text{Fe}^{2+}$  complexes.

### III. DISCUSSION

#### A. Determination of the Sign of the Internal Field in $\text{FeBr}_2$

As shown in Fig. 3 the effect of an applied magnetic field,  $H_a$ , below the flop-field is to split the lines due to  $+\frac{1}{2} \rightarrow +\frac{3}{2}$ ,  $-\frac{1}{2} \rightarrow -\frac{3}{2}$  transitions of ions on different sublattices. We do not initially know which zero-field line belongs to the  $m = +\frac{1}{2} \rightarrow m^* = +\frac{3}{2}$  transition and which to the  $m = -\frac{1}{2} \rightarrow m^* = -\frac{3}{2}$  transition. Nor do we know which sublattice peak is which. However, we may write the shift of each of the two zero-field lines from their center as

$$E_1 = -\frac{1}{2}(3g_1 - g_0)\mu_N H_{\text{eff}}, \quad (2)$$

$$E_2 = +\frac{1}{2}(3g_1 - g_0)\mu_N H_{\text{eff}}, \quad (3)$$

where  $H_{\text{eff}}$  is the effective field at the nucleus,  $\mu_N$  is the nuclear magneton,  $g_0$  and  $g_1$  are the nuclear  $g$  values of the ground and excited states, respectively.<sup>10</sup> To obtain the sublattice splittings we note that for an  $A$  sublattice ion  $H_a$  is in the direction of the ionic moment and it is in the opposite direction for a  $B$  ion. If  $H_i > 0$ , the applied field is in the same direction as  $H_i$  for an  $A$  ion, and

$$H_{\text{eff}} = H_i + H_a \quad \text{for an } A \text{ ion}$$

and

$$H_{\text{eff}} = H_i - H_a \quad \text{for a } B \text{ ion.}$$

Thus the sublattices split, and the line shifts are given

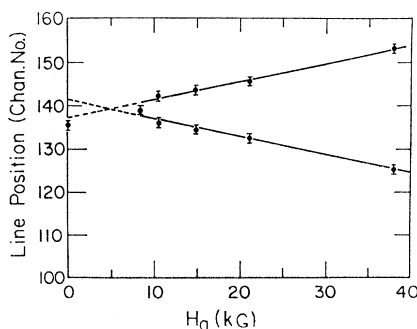


FIG. 4. Position of high-energy line (high velocity) in  $\text{FeCl}_2$  at various applied magnetic fields. (Higher channel numbers correspond to higher velocities.)

by

$$E_1^A = -\frac{1}{2}(3g_1 - g_0)\mu_N(H_i + H_a), \quad (4a)$$

$$E_1^B = -\frac{1}{2}(3g_1 - g_0)\mu_N(H_i - H_a), \quad (4b)$$

$$E_2^A = +\frac{1}{2}(3g_1 - g_0)\mu_N(H_i + H_a), \quad (4c)$$

$$E_2^B = +\frac{1}{2}(3g_1 - g_0)\mu_N(H_i - H_a). \quad (4d)$$

For the four line positions below the flop-field the experimental points coincide well with the theoretical shifts (solid line, Fig. 3). For  $H_i < 0$ , four lines in the same positions are predicted, but this time the effective fields are

$$H_{\text{eff}} = H_i - H_a \quad \text{for } A \text{ sublattice ions,}$$

and

$$H_{\text{eff}} = H_i + H_a \quad \text{for } B \text{ sublattice ions.}$$

Hence the following equivalences:

$$E_1^{A'} = E_1^B, \quad (5a)$$

$$E_1^{B'} = E_1^A, \quad (5b)$$

$$E_2^{A'} = E_2^B, \quad (5c)$$

$$E_2^{B'} = E_2^A, \quad (5d)$$

where the primes refer to the line positions with  $H_i < 0$ . The two possibilities can be distinguished at fields above the flop-field. Since the  $B$  sublattice flops, the sublattice splittings must collapse to the position of the  $A$  sublattice lines, with a small correction for the reversal of the interionic dipole field of the  $B$  sublattice ions. Figure 3 shows that the  $A$  sublattice lines are those which correspond to  $H_i > 0$ .

The above discussion tacitly assumed no change in the internal field after the spin-flop. It is reasonable to suppose that the spin-flop transition does not affect  $H_o$ ,  $H_{\text{orb}}$ , or  $H_{\text{dip}}$ . However, in addition to the intraionic field there is the field at each lattice point due to all the other ions in the crystal,  $H_{\text{dip}'}$ . This interionic dipolar field can be calculated by performing the appropriate lattice sum. The sum will depend on whether the individual dipoles are arranged ferromagnetically or antiferromagnetically. Thus the collapse of the sublattice splitting is not expected to be exactly to the  $A$  position, but to a position differing from it by the difference in the dipole sum for ferromagnetic and antiferromagnetic spin ordering. These dipole sums<sup>12</sup> were calculated for  $\text{FeCl}_2$ ,  $\text{FeBr}_2$  and  $\text{FeI}_2$ , and are listed in Table II. The experimental difference for  $\text{FeBr}_2$ , obtained from Fig. 3, is

$$H_{A-B} - H_{A+B} = -6.7 \text{ kG.}$$

The calculated difference, from Table II, is

$$H_{A-B} - H_{A+B} = -6.8 \text{ kG,}$$

which is in good agreement with the experimental results.

<sup>12</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 2nd ed., Appendix A.

TABLE III. Internal magnetic field  $H_i$ , estimated contact field  $H_o$ , and isomer shifts  $\delta$ , relative to  $\text{FeCl}_2$ .

	$H_i$ (kG)	$H_o$ (kG)	$\delta$ (mm/sec)
$\text{FeCl}_2$	+ 2.8	-419	0.00
$\text{FeBr}_2$	+29.6	-390	-0.03
$\text{FeI}_2^a$	+74.0	-345	-0.049

<sup>a</sup>  $H_i$  and  $\delta$  are from Pfletschinger (Ref. 4).

### B. $\text{FeCl}_2$

Because no sublattice splittings can be observed at fields below the flop-field in this case, one cannot perform the same kind of analysis as in the case of  $\text{FeBr}_2$ . However, the data plotted in Fig. 4 for the splittings above the flop-field would indicate  $H_i < 0$  in the ferromagnetic state ( $H_i \cong -5$  kG from the extrapolated crossover point on Fig. 4). Using the calculated lattice sums we find that  $H_{A-B} - H_{A+B} = -7.9$  kG for  $\text{FeCl}_2$ . Thus the internal field,  $H_i$ , below the spin-flop transition is calculated to be  $\sim +2.8$  kG, which would not lead to a resolvable splitting and so is in agreement with the observed lack of a magnetic hyperfine splitting in  $\text{FeCl}_2$ .

### IV. CONCLUSIONS

The above result (that  $H_i > 0$  in  $\text{FeBr}_2$ ) together with the observation<sup>4</sup> that the internal field increases (in magnitude) on going from  $\text{FeCl}_2$  to  $\text{FeBr}_2$  to  $\text{FeI}_2$  implies that  $H_i > 0$  in  $\text{FeI}_2$  also. Using the experimentally determined electric field gradients,  $q_z$ ,  $\langle S_z \rangle = 1.68$ , and  $\langle L_z \rangle = 0.68$ ,<sup>13</sup> we may calculate values of  $H_{\text{dip}}$  and  $H_{\text{orb}}$ . Then with these values, the experimental values for  $H_i$  and the calculated values of  $H_{\text{dip}'}$  (Table II), we can estimate  $H_o$  for  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ , and  $\text{FeI}_2$ . The results along with the isomer shifts are listed in Table III. A comparison of these values for  $H_o$  with those calculated by Watson and Freeman<sup>10</sup> for various electronic configurations indicates an increasing percentage of 4- $s$  character in the  $\text{Fe}^{2+}$  electronic configuration in going from the chloride to the iodide. This increase would be expected as a result of the covalency of the Fe-halogen bond. The decrease in isomer shift in going from the chloride to the iodide (Table III) is also expected to result from an increasing fraction of 4- $s$  electrons.<sup>14</sup> It is interesting to note that the Fermi contact field is much more sensitive to changes in bonding than is the isomer shift (Table III).

### ACKNOWLEDGMENTS

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<sup>13</sup> J. W. Stout (private communication).

<sup>14</sup> L. R. Walker, G. K. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).