

## Mössbauer Effect in Some Iron-Rare Earth Intermetallic Compounds

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 (Received November 1, 1961)

The magnetic properties of iron in cubic Laves-phase compounds having the  $MgCu_2$  structure have been investigated using the  $Fe^{57}$  Mössbauer effect. The field at the nucleus was found to be  $230 \pm 5$  koe in all compounds except  $CeFe_2$ , where two distinct hyperfine structures were resolved. The results indicate that the configuration of the iron atoms is the same in all these compounds and that the contribution to the hyperfine field by the conduction electron polarization is either very small or else dominated by the iron  $d$  shell. The more complex behavior in  $CeFe_2$  is associated with the transfer of the cerium  $4f$  electron to the iron  $d$  band. The isomer shift indicates that this electron is not localized on a particular iron atom, while the existence of two distinct hyperfine fields suggests that there may be a spatially periodic spin density fluctuation in the  $d$  band.

**E**XPERIENCE with the Mössbauer effect<sup>1</sup> of  $Fe^{57}$  atoms<sup>2</sup> dilutely dispersed in iron,<sup>3</sup> cobalt and nickel,<sup>4</sup> and the copper-nickel alloys<sup>5</sup> has shown that the field at the iron nucleus does not depend strongly on its extra-atomic environment, that is, on the type or the magnetization of its neighboring atoms. This suggests that the  $3d^74s$  atomic configuration of metallic iron<sup>6</sup> is particularly stable and supports the conclusion that the major part of the field arises through the Fermi contact interaction from the exchange polarization of the inner  $s$  electrons by the incomplete  $3d$  shell of the atom itself. It is of considerable interest to extend these studies to iron atoms in other metallic environments where a fuller understanding of the contributions to the field of the nucleus may be obtained.

### INTRODUCTION

A particularly interesting comparison can be made in those cubic Laves-phase compounds of iron and the rare earths which have the  $MgCu_2$  structure.<sup>7,8</sup> Their formula is  $RFe_2$ , where  $R$  stands for a rare-earth atom. It has been found in this series that with one exception the lattice constant is essentially a smooth function of the atomic number of the rare-earth element.<sup>7</sup> The cerium compound has an anomalously small lattice constant which results from the transfer of the  $4f$  electrons from the cerium atoms to the iron  $d$  band. Similar behavior has also been reported for other cerium intermetallic compounds.<sup>9</sup>

The  $RFe_2$  compounds have the structure shown in

<sup>1</sup> R. L. Mössbauer, *Z. Physik* **151**, 124 (1958).

<sup>2</sup> R. V. Pound and G. A. Rebka, Jr., *Phys. Rev. Letters* **3**, 554 (1959); J. P. Schiffer and W. Marshall, *ibid.* **556** (1959).

<sup>3</sup> S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, *Phys. Rev. Letters* **4**, 28 (1960).

<sup>4</sup> G. K. Wertheim, *Phys. Rev. Letters* **4**, 403 (1960), see also C. E. Johnson, M. S. Ridout, T. E. Cranshaw, and P. E. Madsen, *Phys. Rev. Letters* **6**, 450 (1961).

<sup>5</sup> G. K. Wertheim and J. H. Wernick, *Phys. Rev.* **117**, 714 (1961).

<sup>6</sup> J. H. Wood, *Phys. Rev.* **117**, 714 (1960).

<sup>7</sup> J. H. Wernick and S. Geller, *Trans. Am. Inst. Mining, Met. Petrol. Engrs.* **218**, 866 (1960).

<sup>8</sup> The Mössbauer effect in isostructural  $UF_2$  has recently been reported by S. Komura *et al.*, *J. Phys. Soc. Japan* **16**, 1479 and 1486 (1961).

<sup>9</sup> See references cited in reference 7 above.

Fig. 1. The rare-earth atoms (open circles) occupy positions of the diamond structure. The iron atoms (shaded circles) form a corner-sharing tetrahedral network. The space group is  $O_h^7 - Fd\bar{3}m$ , with eight formula units in a unit cell. For the interpretation of the Mössbauer data the most important feature is the point symmetry of the iron sites which is  $\bar{3}m$ . An examination of the figure shows that all iron atoms are equivalent and that the threefold axes lie in (111) directions. The iron nuclei may consequently experience an axially symmetric field gradient.

### EXPERIMENTAL

The samples were prepared by induction melting stoichiometric amounts of iron and the rare-earth element in an argon atmosphere in a quartz crucible. In the case of the samarium compound essentially clean samples were obtained when excess samarium was provided to compensate for its high vapor pressure. X-ray powder photographs were taken of the resulting materials to confirm that the desired compound had been formed. Absorbers for the Mössbauer experiments were

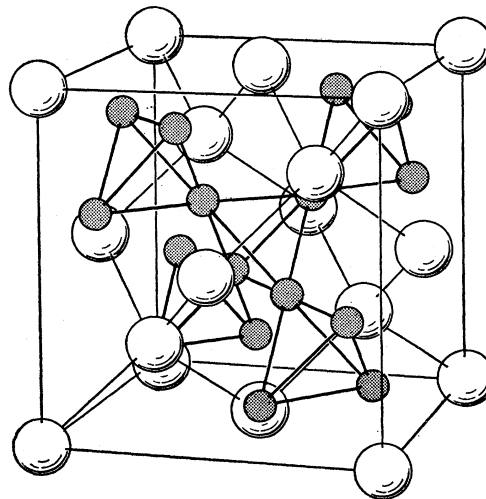


FIG. 1. The structure of  $RFe_2$ .  $R$ —rare-earth atom (open);  $Fe$ —iron atom (shaded).

made by crushing small amounts of the compound in a nitrogen atmosphere. The resulting powder was cemented to a 0.005-in.-thick sapphire substrate. This in turn was clamped to a copper sample holder, surrounded by a thin aluminum radiation shield, and placed in a vacuum dewar.

The "unsplit" source consisted of a piece of type 310 stainless steel into which  $\text{Co}^{67}$  has been diffused.<sup>4</sup> The source was attached to a loudspeaker voice coil which executed approximately parabolic motion. The 14.4-keV gamma rays penetrating the absorber were selected with a conventional single-channel, scintillation-counter spectrometer whose output was amplitude modulated with a voltage proportional to the instantaneous velocity of the source. The resulting pulse height spectrum was sorted by a 256-channel analyzer.

### RESULTS AND DISCUSSION

The results obtained may be divided into two types: those for  $\text{CeFe}_2$  shown in Fig. 2(a); and those characteristic of all the other compounds, of which two examples are given in Figs. 2(b) and (c).

We will discuss first the simple six-line pattern obtained in all but the case of  $\text{CeFe}_2$ . It has been pointed out above that crystallographically the iron atoms are all equivalent. However, since we are dealing with a ferrimagnetic material<sup>10</sup> in which the magnetization of the domains may be randomly oriented with respect to the four  $\langle 111 \rangle$  axes of the electric field gradient tensors, we may expect the absorption lines to be broadened by an amount comparable to the quadrupole coupling. The data are in accord with these facts. The absorption lines are broad and weak, but conform approximately to the pattern expected in the absence of quadrupole interaction. The results obtained for the various compounds

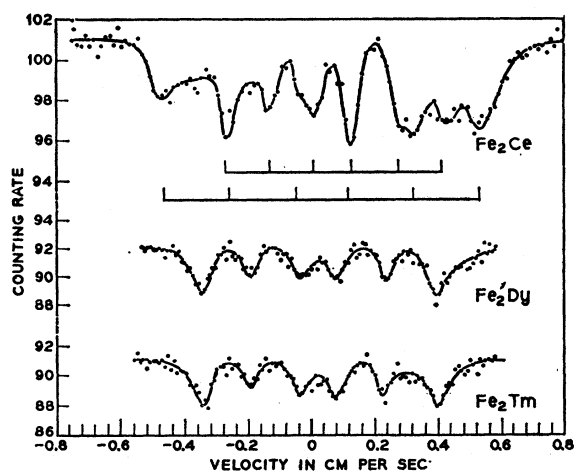


FIG. 2. The hyperfine structure of the 14.4-keV gamma transition of  $\text{Fe}^{67}$  in (a)  $\text{CeFe}_2$ , (b)  $\text{DyFe}_2$ , and (c)  $\text{TmFe}_2$ , measured at 78°K.

<sup>10</sup> E. A. Nesbitt, J. H. Wernick, and E. Corenzwit, *J. Appl. Phys.* **30**, 365 (1959).

measured (Table I) show that the field at the iron nucleus at low temperature in all these compounds approximates 230 koe.

This is a surprising result because it shows that the field at the iron nucleus does not depend to a measurable extent on the magnetic properties of the rare-earth atoms whose  $f$ -shell configurations differ widely, Table II. It requires that the atomic configuration of the iron atoms in all these compounds be the same, and indicates that the contribution to the field at the nucleus made by the conduction electron polarization is either negligibly small or, more likely, identical in all compounds. Such a similarity could arise only if the conduction electron polarization at the iron nucleus arises largely from interaction with the  $d$  electrons of the iron atoms themselves and to a lesser extent from interaction with the  $4f$  electrons of the rare-earth atoms. Such a behavior is consistent with the interpretation recently given for the La Knight shift in isostructural compounds.<sup>11</sup>

The value of 230 koe found for the field at the iron nucleus at low temperature in all the compounds is not within the range of those previously reported in  $3d$ -group metallic environments. These range from 340 koe in iron itself down to 260 koe in a copper-nickel alloy of low magnetization (40 at. % Cu). The observed differences may in large part arise from the conduction-electron polarization and do not necessarily require changes in the configuration of the iron atom. The smaller value of the field could arise from a change of sign of the conduction-electron polarization relative to that in metallic iron. It could also result, in part, from a decrease in the moment of the iron  $d$  shell.

The isomer shifts in these compounds at room temperature average 0.01 cm/sec measured relative to stainless steel. This value is equal to that reported for iron dissolved in the  $d$ -group metals<sup>12</sup> and is an indication that the configuration of the iron is similar in the two cases. (It is considered unlikely that major changes in configuration which exactly compensate insofar as the charge density at the nucleus is concerned take place.)

Both the field of the nucleus and the isomer shift thus indicate that the  $d$  band associated with the iron sublattice has properties similar to that of metallic iron. There is little or no tendency for electrons from the rare-earth atoms to fill the partially empty  $d$  band, a conclusion which parallels that reached in the discussion of iron dissolved in the Cu-Ni alloys.<sup>5</sup>

We now consider results obtained with a  $\text{CeFe}_2$  absorber. These are considerably more complicated, as may be seen in Fig. 2(a). The data may, however, be separated into two six-line patterns on the assumption that both will exhibit negligibly small quadrupolar line shifts. The resulting six-line patterns are indicated directly below the data. The intensities are in reasonable

<sup>11</sup> V. Jaccarino (private communication).

<sup>12</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

TABLE I. Magnetic properties of some iron-rare earth cubic Laves-phase compounds.

	<i>H</i> at nucleus (koe)		Isomer shift (cm/sec)		Saturation magnetization $\mu_B$ /formula unit		Curie temp. °K
	298°K	78°K	298°K	78°K	Meas.	Comp.	
CeFe <sub>2</sub>	...	{212} <sup>a</sup> {312}	...	{0.063} <sup>b</sup> {0.031}	6.97	(c)	878
SmFe <sub>2</sub>	...	~220	...	~0.05	...	5.15	674
GdFe <sub>2</sub>	...	...	...	...	...	2.56	813
DyFe <sub>2</sub>	216	228	0.007	0.024	5.44	5.56	663
HoFe <sub>2</sub>	188	226	~0.01	0.022	6.02	5.56	608
ErFe <sub>2</sub>	189	232	0.010	0.019	5.02	4.56	473
TmFe <sub>2</sub>	...	231	...	0.025	2.92	2.56	613

<sup>a</sup> The uncertainty in the measured field values is  $\pm 4$  koe.

<sup>b</sup> The uncertainty in the isomer shifts is  $\pm 0.004$  cm/sec.

<sup>c</sup> The magnetization of the cerium compound cannot be computed since the moments of the two types of iron atoms are not known.

accord with those expected. The field corresponding to the smaller splitting is 212 koe, which is only slightly smaller than that found in the compounds discussed above. The field corresponding to the other hf structure is 312 koe.

The Mössbauer experiment, thus, clearly shows the presence of two distinct types of iron in CeFe<sub>2</sub>. From the x-ray diffraction point of view, on the other hand, this compound is indistinguishable from the others. This means that the two types of iron can differ only magnetically. The explanation previously given<sup>7</sup> for the lattice contraction is that the 4*f* electrons of the cerium atoms are transferred to the *d* band associated with the iron sublattice. Since there are two iron atoms for each rare-earth atom this could result in two nonequivalent types of iron if these electrons are each localized near a particular iron atom.

The isomer shifts associated with the two distinct types of iron differ by only 0.032 cm/sec, the larger shift going with the smaller field. This is consistent with the notion that an increase in the *d*-electron density will increase the shift while decreasing the moment of the *d* shell and hence the field at the nucleus. However, the magnitude of the change in the isomer shift is much smaller than that expected for the addition of one *d* electron indicating that the interpretation based on a localized *d* electron cannot be correct.

This is also apparent from the data on the field at the nucleus since the addition of one electron to the already more than half-filled *d* band should, in the simplest picture, reduce the moment of the iron atom and cannot account for the larger, 312-koe field. (It is assumed here that the smaller field which is similar in magnitude to that found in the other compounds results from the unperturbed iron atom.)

The small difference in isomer shift between the two types of iron indicates that the charge density at the nucleus is similar at both sites; the large difference in the field indicates that the spin density at the nucleus differs by an amount corresponding to about one electron-spin in the *d* band. This picture is consistent with the suggestion due to Jaccarino that the electron lost

by the cerium atom enters the *d* band of the iron sublattice in such a way as to contribute almost equal amounts of charge density at all iron atoms. At the same time there must arise a spatially periodic spin-density fluctuation which has characteristic values at the iron atoms and produces the two distinct fields which were observed. It is planned to check this suggestion by neutron diffraction.

#### BULK MAGNETIC PROPERTIES

The low-temperature saturation magnetization and the Curie temperature of these compounds have been measured by H. J. Williams and E. A. Nesbitt,<sup>13</sup> respectively, and are also given in Table I. The saturation magnetization indicates that the behavior of these compounds is similar to that of other rare-earth intermetallics which have been previously studied. In these compounds it was found that the saturation magnetization may be approximately computed by combining the moment, *gJ*, of the rare-earth atom computed for the 4*f* shell with the known moment of the other element (here 2.22  $\mu_B$ /iron atom) on the assumption that the coupling between the iron moment and the rare-earth spin is antiferromagnetic.<sup>14</sup> (The orbital angular momentum is antiparallel to the spin for the less than half-filled shell and parallel for the more than half-filled

TABLE II. Magnetic properties of the 4*f* shell of some rare-earth atoms.

	<i>S</i>	<i>L</i>	<i>J</i>	<i>g</i>	<i>gJ</i>
Ce	1/2	3	5/2	6/7	2.14
Sm	5/2	5	5/2	2/7	0.71
Gd	7/2	0	7/2	2	7
Dy	5/2	5	15/2	4/3	10
Ho	2	6	8	5/4	10
Er	3/2	6	15/2	6/5	9
Tm	1	5	6	7/6	7

<sup>13</sup> The authors are indebted to H. J. Williams and E. A. Nesbitt for permission to quote these results prior to publication.

<sup>14</sup> H. J. Williams, J. H. Wernick, E. A. Nesbitt, and R. C. Sherwood (to be published).

shell.) The values obtained from this calculation are also given in Table I and agree with the measurements to within  $0.5 \mu_B$ /molecule, indicating that the atomic configurations of the rare-earth and iron atoms are not very different from those assumed in the calculations.<sup>15</sup> This conclusion is in agreement with that reached on the basis of the Mössbauer experiments.

The measured Curie temperatures are all sufficiently high so that the magnetic fields determined at 78°K are a good approximation to the 0°K values. This is borne out in the case of the  $\text{HoFe}_2$  sample where Mössbauer measurements were also made at 4°K yielding a field only 3% higher than that found at 78°K.

### CONCLUSIONS

These measurements have shown that the fields at the iron nucleus in the  $R\text{Fe}_2$  compounds (except  $\text{CeFe}_2$ ) are all very similar. This indicates a corresponding similarity

<sup>15</sup> The agreement between the measured and the calculated values is improved if a somewhat smaller value is used for the magnetic moment of the iron atom.

in the atomic configurations and suggests that the contribution to the field made by the conduction electron polarization is either small or, more likely, dominated by the interaction with the iron  $d$  electrons. The isomer shift indicates that the configuration is like that of metallic iron. Measurements of the magnetization confirm that the magnetic properties of the iron atoms in these compounds are similar to those of iron in its natural lattice. In the case of  $\text{CeFe}_2$  the Mössbauer effect shows the presence of two magnetically non-equivalent types of iron. These are thought to result from the transfer of the cerium  $4f$  electron to the iron  $d$  band. The isomer shift indicates that these electrons are not localized on particular iron atoms. It is suggested that the two magnetically distinct types of iron arise from a spatial spin-density fluctuation in the  $d$  band.

### ACKNOWLEDGMENTS

The authors would like to thank V. Jaccarino for stimulating discussions and for a reading of the manuscript, and D. N. E. Buchanan for assistance with the measurements.

## Spin Waves in Exchange-Coupled Complex Magnetic Structures and Neutron Scattering

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(Received September 18, 1961)

In this paper, we develop a spin-wave theory of the Holstein-Primakoff type for exchange-coupled crystals with an arbitrary number  $n$  of magnetic ions per primitive magnetic unit cell, when the resultant electronic spin vectors of these ions are mutually parallel or antiparallel in a given domain, except for spin-wave fluctuations. A simple and systematic method is presented for finding a complete set of normal spin-wave modes. This method is used to derive a convenient formula for the component of the total electronic spin vector of the magnetic ions in a domain along the axis of spin alignment. We show that there exists at least one "acoustic" branch among the  $\leq n$  distinct branches of the spin-wave spectrum when the magnetic anisotropy and external magnetic field contributions vanish. For the case when all the  $m \geq 1$  acoustic branches existing in the absence of these contributions are identical, we prove that the acoustic spin-wave energies corresponding to a given wave-number vector  $\mathbf{k}$  are of  $O(|\mathbf{k}|^{2/m})$  for  $|\mathbf{k}| \rightarrow 0$ . The situation in which a single acoustic branch exists when no external magnetic field or anisot-

ropy effects are present is studied in detail and, under suitable restrictions, an explicit formula is derived for the energies of the magnons of this branch for  $|\mathbf{k}| \rightarrow 0$ . We apply this spin-wave theory to obtain general cross-section formulas for the one-magnon zero-phonon scattering of neutrons by the class of exchange-coupled crystals referred to in the first sentence of this abstract, when the magnetic ions in these crystals are completely quenched orbitally. The formulas in question are used to predict a spin-wave phenomenon of wide generality for polarized incident neutrons. This phenomenon is of particular experimental interest in connection with the acoustic spin-wave scattering of such neutrons by crystals of this class having a single acoustic branch and has been qualitatively confirmed by experiments on magnetite. For the last-mentioned crystals, we use an exact limit result of this paper to suggest a simple approximate form of the general cross-section equations pertaining to acoustic spin-wave scattering, when only magnons of sufficiently small  $|\mathbf{k}|$  are of interest.

### I. INTRODUCTION

**I**N this paper, we employ a formalism which is a natural generalization of that of Holstein and Primakoff<sup>1</sup> to construct a spin-wave theory applicable

to exchange-coupled crystals<sup>2</sup> with an arbitrary number of magnetic ions per primitive magnetic unit cell. We apply this theory to the spin-wave scattering of neutrons of any initial polarization by such crystals for the case

<sup>1</sup> T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

<sup>2</sup> The term "exchange" is employed in this paper to denote both ordinary exchange and superexchange, it being hoped that no confusion will be caused by this usage.