nearly filled. This would produce a resistance maximum, as observed on Cr and Cr-Fe alloys.[10] A nearly filled s-electron subband would also explain the large positive R_H value near chromium in the antiferromagnetic alloys. The first term in Eq. (1) would change to $\sigma_{2u'}{}^2/\sigma^2\nu_h(t_{2u'})Ne$, where $\sigma_{2u'}$ would be the conductivity of the sub-band $t_{2u'}$ and $\nu_h(t_{2u'})$, the number of holes in the $t_{2u'}$ sub-band, would decrease to zero, giving a large R_H contribution.

On the other hand, Goodenough (private communication) suggests that the t_{2u} and t_{2g} electrons have orbitals of similar symmetry, so that they tend to mix. They form essentially a single band, where the electronic density of state is given by the sum of t_{2u} and t_{2g} states. This band can be approximated by a single parabolic band left of the minimum in the density of state curve of chromium. The effective number of holes in this parabolic band can become very small near chromium, giving a large R_H value.

ACKNOWLEDGMENTS

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Anisotropic hfs Interactions in Ferromagnets from Mössbauer Effect Studies

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The anisotropy of the magnetic hyperfine interaction in ferromagnetic $ZrFe_2$ has been demonstrated with the Mössbauer effect. It is suggested that such anisotropy is responsible for the failure to observe domain-wall enhanced NMR in similar materials. It may also account for the failure to detect the NMR of iron atoms with impurity neighbors in dilute ferromagnetic alloys. These atoms are easily seen in Mössbauer effect studies.

INTRODUCTION

RECENT Mössbauer effect (ME) studies of dilute iron alloys have shown that the hyperfine structures of iron atoms with impurity atoms in the near- and next-near-neighbor shells are readily resolved.[1] These configurations have not been detected in nuclear magnetic resonance (NMR) experiments on similar alloys. Attempts to observe the NMR of Fe^{57} in certain intermetallic compounds have been similarly unsuccessful[2] despite the fact that the hfs fields were accurately known from ME studies.

We suggest that the difficulties encountered in domain-wall-enhanced NMR are a direct result of the effects of an anisotropic magnetic hfs interaction which is allowed when the Fe occupies a site of noncubic point symmetry. From a ME study in the particular ferromagnet $ZrFe_2$ we will show that the anisotropy exceeds 7%, an amount that would make the observation of NMR difficult at best. The implications that this has for NMR and ME observation in Fe alloys will be considered.

To see the effects that anisotropy produces on domain-wall enhanced NMR in a ferromagnet, let us consider a simple example, that of uniaxial anisotropy. We choose a uniaxial crystal in which the easy axis of magnetization coincides with the c axis, and let this axis be the z axis of our coordinate system. If we consider a domain wall in which the spins lie in the xz plane, Fig. 1, then the local fields at the nuclei will vary as a function of the y coordinate in the wall provided *the hfs interaction is anisotropic.* If $H_{\text{hfs}}=\mathbf{I}\cdot\tilde{A}\cdot\mathbf{S}$ with $A_z\neq A_x=A_y$, then the fractional variation of the hyperfine field $\Delta H/H$ is equal to $C(A_z-A_x)/A_z$, where C is a number of order unity. (Detailed NMR lineshape analyses have been made for anisotropic hfs interactions in magnetite, where the resonances are enhanced by domain rotation.[3])

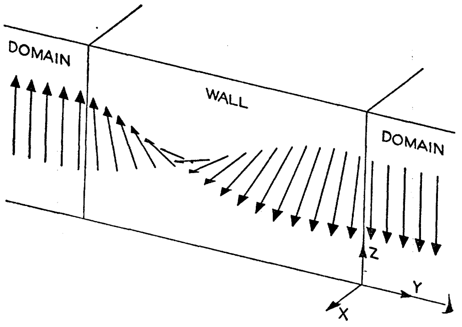

Fig. 1. Change in the direction of magnetization within a domain wall lying in the xz plane of a uniaxial crystal.

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[1] G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Letters **12**, 24 (1964).

[2] A. C. Gossard and V. Jaccarino (private communication).

[3] E. L. Boyd and J. C. Slonczewski, J. Appl. Phys. **33**, 1077S (1962).

In the ME, on the other hand, the nuclei in the domains rather than those in the walls make the primary contribution, simply because the number of atoms in the domains far exceeds the number in the walls. The atoms in the domains all experience the same hf interaction since each spin **S** is in a definite crystallographic direction and consequently no broadening is to be expected. Conceptually, the anisotropy of the hfs interaction would be most directly demonstrated in an oriented single crystal in which the magnetization can be turned to simple crystallographic directions with an external magnetic field. However, under certain conditions, the anisotropy may be observed even in a polycrystalline sample. For example, since the magnetization in a randomly oriented polycrystalline sample lies along prescribed crystalline axes (easy directions) the application of an external field sufficient to saturate the whole sample in an arbitrary spatial direction will result in the spins in different crystallites having random orientation with respect to the crystalline axes. Anisotropy of the hfs interaction will then manifest itself as line broadening.

The intermetallic compounds, $ZrFe_2$, $TmFe_2$,[4] etc., have an additional feature which allows demonstration of the anisotropy, even without an external field. In these cubic Laves phase metals the iron atoms lie on a corner-sharing, tetrahedral network, Fig. 2. The point symmetry at any iron atom is $\bar{3}m$. The threefold axes lie in [111] directions. The iron atoms are crystallographically equivalent provided the crystal is not magnetized. The presence of a magnetic axis renders them distinguishable because the angle θ between the axis of the axially symmetric field gradient and the magnetic field will not, in general, be the same for all iron atoms. If the easy direction of magnetization is [111] there are two classes of iron atoms to be distinguished; those with θ equal to 0 and those with θ equal to 70°32′, Fig. 3. They are present in the radio of 1:3, and can be distinguished in a Mössbauer experiment since the combined effect of magnetic dipolar and electric quadrupolar interactions is dependent on the angle θ,[5] regardless of whether there is anisotropy in the *magnetic* hfs interaction or not.

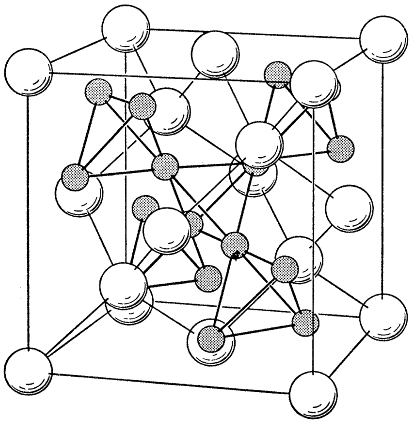

FIG. 2. The cubic Laves phase structure. The iron atoms occupy the shaded sites. The other atoms lie on a diamond lattice.

EXPERIMENTAL

To demonstrate this effect an absorber was made of finely crushed $ZrFe_2$ incorporated into an epoxy binder to prevent physical rotation of the particles when a magnetic field was applied. The single phase $ZrFe_2$ was prepared by inert electrode arc melting in a water-cooled copper crucible. A second absorber was made of $TmFe_2$ prepared by induction melting in a quartz crucible in argon. The radioactive source was Co^{57} in Cu. The apparatus was similar to one previously described.[6] The magnetic field was obtained with a Westinghouse NbZr superconducting solenoid.

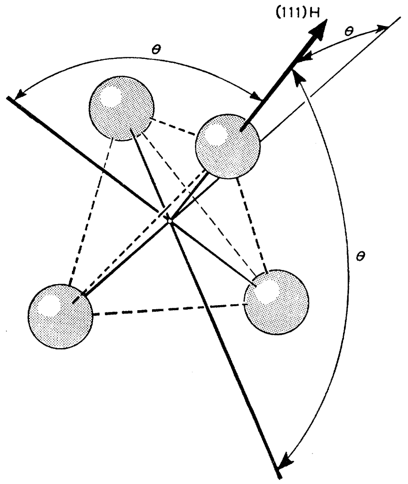

FIG. 3. Angular relationship between direction of magnetization and axes of symmetry for one of the tetrahedra of iron atoms of Fig. 2. The solids lines are the four threefold symmetry axes which lie in [111] directions. The magnetization—solid arrow—is shown to lie along *one* of the [111] directions.

RESULTS AND DISCUSSIONS

(a) $ZrFe_2$

The absorption obtained with the sample at 4°K, Fig. 4, shows the presence of two superimposed hf spectra, which are indicated below the data. The ratio of intensities is approximately 1:3 as expected for a [111] easy direction of magnetization. The weaker spectrum, for which the axes of the electric field gradient tensor and the magnetic field are parallel, is readily

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[4] J. H. Wernick and S. Geller, Trans. AIME **218**, 866 (1960).

[5] In earlier Mössbauer experiments on RFe_2 compounds, these two distinct hyperfine structures were not resolved, but the absorption lines were reported to be broadened.

[6] R. L. Cohen, P. G. McMullen, and G. K. Wertheim, Rev. Sci. Instr. **34**, 671 (1963).

analyzed, since the quadrupolar displacement of all lines is of the same magnitude. The values of the hyperfine field, H, quadrupole splitting, e^2qQ, and isomer shift, IS, are shown in Table I. The stronger spectrum was analyzed using the computation of Parker[7] interpolated for $\theta=70°32'$.[8]

It should be noted that the hyperfine fields for the two sites differ by 7.6%. For the relatively small quadrupolar admixture, $\lambda=e^2qQ/4\mu H<0.1$, the position of the outer lines remains a good measure of the magnetic hf coupling. In the linear approximation where the energy eigenvalues are given by

$$E_M=\frac{\mu HM}{I}+(-1)^{|M|+1/2}e^2qQ\times\left(\frac{3M^2-I(I+1)}{4I(2I-1)}\right)\left(\frac{3\cos^2\theta-1}{2}\right), \quad (1)$$

the quadrupolar displacements for $M=+\frac{3}{2}$ and for $M=-\frac{3}{2}$ are the same and no error is introduced by using the outer lines to determine the hf field. In Parker's calculation for $\lambda=0.1$ the distance between $E_{+\frac{3}{2}}$ and $E_{-\frac{3}{2}}$ is increased by a maximum of 1.3% above the pure magnetic splitting for any value of θ. There is consequently no possibility that the observed difference in hyperfine field arises from quadrupolar admixture.

TABLE I. Fe^{57} hfs parameters of $ZrFe_2$ at 4°K.

	θ 70°32′	0°
Ground-state splitting	0.264 cm/sec	0.244 cm/sec
Excited-state splitting	0.135	0.190
	0.1515	0.139
	0.170	0.091
e^2qQ, Quadrupole coupling	0.11±0.01	0.10±0.01
Hyperfine field	223 kOe	206 kOe
Isomer shift [$K_4Fe(CN)_6=0$]	-0.0031_5 cm/sec	

The quadrupolar line displacement for $\theta=70°32'$ is $-\frac{1}{3}$ times that for $\theta=0$ according to Eq. (1) and only slightly different in Parker's calculations. The observed values are in the proper ratio and exhibit the difference in sign, giving further assurance that the data have been properly analyzed.

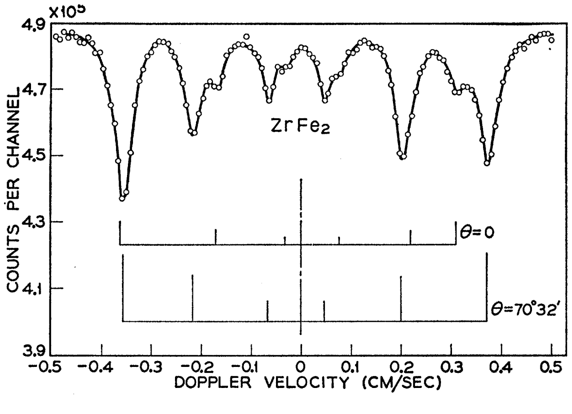

FIG. 4. Mössbauer effect hyperfine splitting of Fe^{57} in $ZrFe_2$ at 4°K. Two distinct hyperfine patterns are indicated. The zero of the Doppler velocity scale corresponds to $K_4Fe(CN)_6\cdot 3H_2O$ which is a convenient, stable reference substance.

From a casual glance at Fig. 4 one might suspect that the two hf patterns exhibit an isomer shift[9] with respect to each other. However, a careful determination of the centroid using a 3:2:1:1:2:3 weighting shows that they coincide to within 0.2 channels. This result lends further support to the correctness of the line assignment since no shift is to be expected inasmuch as the atoms differ only with respect to the direction of spin magnetization.

When an external field sufficient to saturate the magnetization is applied,[10] the well-resolved structure obtained in the absence of the field disappears, Fig. 5. The line at negative Doppler velocity does not broaden

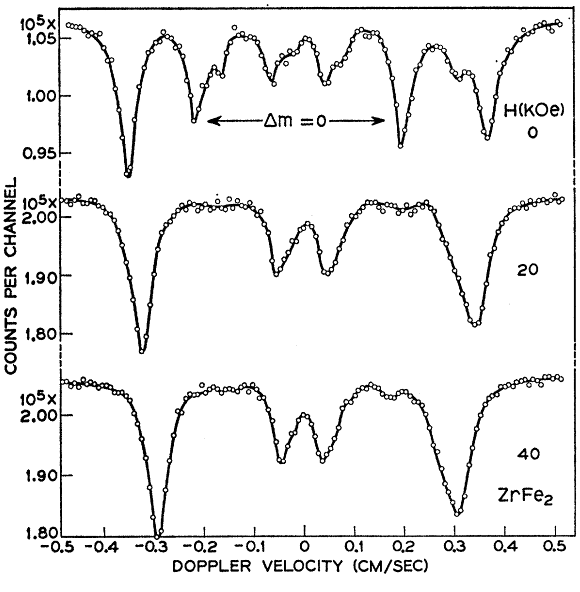

FIG. 5. Effect of turning the magnetization of $ZrFe_2$ to random crystallographic directions is demonstrated by application of a magnetic field sufficient to saturate a polycrystalline sample. (See footnote 10.)

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[7] P. M. Parker, J. Chem. Phys. **24**, 1096 (1956).

[8] The analysis was carried out in the following manner, starting with the position of the six lines. The separation of lines 2 and 4 or 3 and 5 gives the ground-state splitting and hence the hyperfine field. The separation of lines 1 and 2; 2 and 3, or 4 and 5; and of lines 5 and 6 gives the excited state splitting. This is compared with the splitting for $I=\frac{3}{2}$ interpolated for $\theta=70°32'$ from the table of Parker, yielding $\lambda=e^2qQ/4\mu H=0.124$. The quadrupolar line shift is not the same for the four magnetic sublevels of the excited state. Moreover, the total splitting of the excited state is increased somewhat over that for $eq=0$.

[9] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960); L. R. Walker, G. K. Wertheim, and V. Jaccarino, *ibid.* **6**, 98 (1961).

[10] The magnetic field is applied parallel to the direction of the gamma rays. As a result the $\Delta M=0$ transitions, whose radiation pattern has vanishing intensity along the axis of quantization, are sensitive indicators which show when saturation is reached.

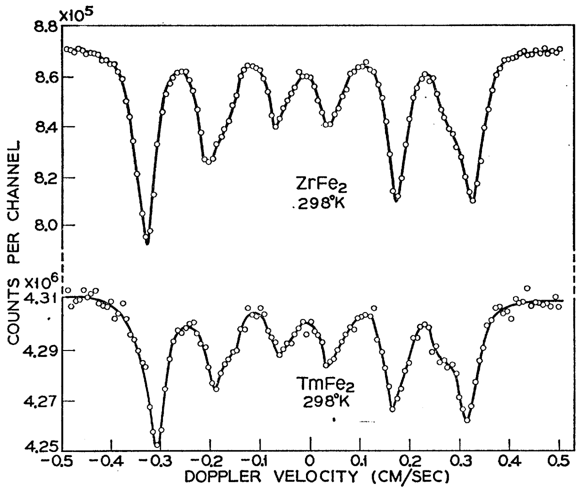

FIG. 6. Comparison of the Mössbauer effect hyperfine structure at 298°K in $ZrFe_2$ and $TmFe_2$. The latter has a somewhat smaller hf field. The resolution of the two types of iron in each spectrum is significantly worse than at lower temperature, perhaps because of reduced magnetocrystalline anisotropy.

appreciably, indicating that other values of θ give line positions intermediate or close to those obtained for $\theta=0°$ and 70°. The structure in the line at highest positive Doppler velocity has been replaced by a broadening which encompasses approximately the same energy as the original splitting, indicating that the 0° and 70° line position give a measure of the total anisotropy in the hfs interaction.[11] *Note added in proof.* To test the conclusions drawn from the ME studies Dr. E. D. Jones has kindly searched for the Fe^{57} NMR in $ZrFe_2$ at 4.2°K. The failure to find a resonance is in keeping with the conclusions drawn here.

(b) $TmFe_2$

$TmFe_2$ was examined[11] to determine whether the presence of an ion with a magnetic moment in the Zr sites would produce additional anisotropy. A comparison of the ME data for $ZrFe_2$ and $TmFe_2$ at 298°K, Fig. 6, shows only a minor difference in the hfs. This is in accord with the earlier finding that neither the Curie temperature nor the hyperfine field in the RFe_2 cubic Laves phase compounds varies appreciably when various rare earth or other elements occupy the R sites.[12–15]

TABLE II. Temperature dependence of H_{eff} in $ZrFe_2$ and $TmFe_2$. The Curie temperatures of these two compounds are 586°K[a] and 613°K. The earlier measurements on $ZrFe_2$, Refs. 12, 13, and 14, gave 206, 190, and 183 kOe for the room-temperature field. These should be compared with $H_{\theta=70°32'}$ which dominates the hf spectrum.

Compound	Temperature (°K)	Hyperfine field (kOe) $\theta=70°32'$	$\theta=0$
$ZrFe_2$	4	223	206
	78	220	204
	298	200	Not determined
$TmFe_2$	78	216	202
	298	191	Not determined
	375	176	Not determined
	473	145	Not determined

[a] The authors are indebted to E. A. Nesbitt for the measurement of the Curie temperature of $ZrFe_2$.

It is also not unexpected in view of the weak coupling between the iron and rare-earth sublattices found in $TmFe_2$.[16]

At 78°K the data for both compounds closely resemble those shown in Fig. 4 for $ZrFe_2$ at 4°K. The chief difference between the two lies in a somewhat smaller magnetic hfs interaction in $TmFe_2$, Table II. The Tm sublattice thus does not contribute in a measurable way to the anisotropy of the iron hyperfine interaction. The origin of the small but significant difference in the hyperfine fields has not been explored.

DILUTE IRON ALLOYS

Considering the greater complexity of the Mössbauer spectra observed in the dilute iron alloys, it is not surprising to find that it has not been possible to demonstrate the anisotropy in the hfs which may be present for Fe atoms with one or more near-neighbor or next-near-neighbor impurity atoms. In spite of this inability to observe anisotropy in ME experiments, we are forced to believe that the failure to detect NMR in these alloys is the result of anisotropy in the hfs. It would be interesting to verify this by doing NMR experiments on single domain particles of these alloys.

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We are indebted to Dr. A. C. Gossard for several discussions and to D. N. E. Buchanan for assistance with the experiments.

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[11] The data also show that the hyperfine field is negative (the application of an external field decreases the hfs). The decrease is equal to the full value of the applied field, i.e., $dE/dH=\mu_{\mathrm{Fe}^{57}}$.

[12] G. K. Wertheim and J. H. Wernick, Phys. Rev. **125**, 1937 (1962). Attempts to further examine the compound $CeFe_2$, whose Mössbauer effect was also reported in this reference have been frustrated by difficulties in reproducing this cubic Laves phase material which forms peritectically from the melt. It appears likely that the original compound was not of the structure or composition claimed.

[13] W. E. Wallace and L. M. Epstein, J. Chem. Phys. **35**, 2238 (1961).

[14] C. W. Kocher and P. J. Brown, J. Appl. Phys. Suppl. **33**, 1091 (1962).

[15] S. Komura and N. Shikazono, J. Phys. Soc. Japan **18**, 323 (1963); S. Komura (to be published).

[16] R. L. Cohen, Phys. Rev. **134**, A94 (1964).