Mössbauer Effect of Fe^{57} in a Cobalt Single Crystal*

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The Mössbauer effect of Fe^{57} in a single crystal of cobalt has been observed. The quadrupole coupling e^2Qq was measured to be -0.064 mm/sec, and the hyperfine field was found to be isotropic and equal to -316.6 ± 2.5 G. The significance of these results is discussed in relation to the theory of hyperfine fields in metals. The ratio of the magnetic moments of the excited and ground states of Fe^{57} was measured to be 1.7135 ± 0.0015.

I. INTRODUCTION

THE study of the effects of the asymmetrical distribution of charge and spin density in metals is of interest for the understanding of the metallic state. Because cobalt in its stable form at ordinary temperatures has hexagonal and not cubic symmetry it is expected to show anisotropic properties, and this paper describes measurements of anisotropic charge and spin densities for very dilute Fe^{57} in a cobalt single crystal using the Mössbauer effect. A brief report of the results of these measurements has been given previously.[1]

The quadrupole splitting of the 14.4-keV state of Fe^{57} enables us to determine the asymmetry of the charge density due to the $3d$ electrons in the unit cell of the iron atom. The corresponding asymmetry in the spin density would be expected to give rise to a dipolar contribution to the hyperfine field so that the hyperfine field would be anisotropic, but it has been found difficult to isolate this effect in the presence of the other contributions to the hyperfine field. Marshall[2] estimated the dipolar field in hexagonal cobalt to be $+83$ kG. However, this was based on a somewhat unrealistic crystal-field potential and it was shown to be much too large by measurements which showed that the hyperfine fields in the cubic and hexagonal forms were very nearly equal.[3] More exact NMR measurements by Koi, Tsujimura, Hihara, and Kushida[4] showed that the hyperfine field is larger in the hexagonal phase, but it is not a simple matter to deduce the dipolar field from these data as it is not known how the other contributions from the orbital angular momentum and the spin density change from one phase to the other. In the present experiments, therefore, we have attempted to observe the dipolar field directly by turning the spins perpendicular to the direction of easy magnetization with a magnetic field and measuring the effect on the hyperfine field.

Incidental to the main purpose of the work we have also obtained (a) an accurate measurement of the ratio of the magnetic moments of the ground and excited states of Fe^{57}, (b) a measurement of the hyperfine field in hexagonal cobalt, and (c) a test of the additivity at the nucleus of the internal and an external field.

2. EXPERIMENTAL DETAILS

The measurements were performed in zero field and in an external magnetic field of 20 kG applied in turn parallel to and perpendicular to the c axis. The crystal was a square plate with 6 mm sides and 0.5 mm thick. The c axis was parallel to one of the 6-mm edges. With this shape the demagnetizing field was small and the same for the two magnetization directions. Co^{57} together with inactive cobalt carrier was electroplated epitaxially upon one of the square faces and was used as the source in the Mössbauer effect measurements: sodium ferrocyanide (made from enriched Fe^{57}) was used as a monoenergetic absorber, so that the resulting spectrum gave the energies of the Fe^{57} in the cobalt crystal. It is essential for the success of the experiment that the Co^{57} source material occupy regular sites in the hexagonal crystal. A description of the plating process has been given.[5] It is based on the observation[6] that low current densities favor deposition of the hexagonal form while high densities result in a mixture of cubic and hexagonal. The Mössbauer effect itself furnishes the best test for epitaxiality. Because of the high anisotropy of the hexagonal crystal, the domains and hence the internal fields are aligned parallel to the c axis in the absence of an external field. If the crystal is viewed at nearly grazing incidence with the c axis nearly along

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[5] G. J. Perlow, in *Proceedings of the Second International Conference on the Mössbauer Effect, Saclay, France, 1961*, edited by D. M. J. Compton and A. H. Schoen, (John Wiley & Sons, New York, 1962), p. 76.

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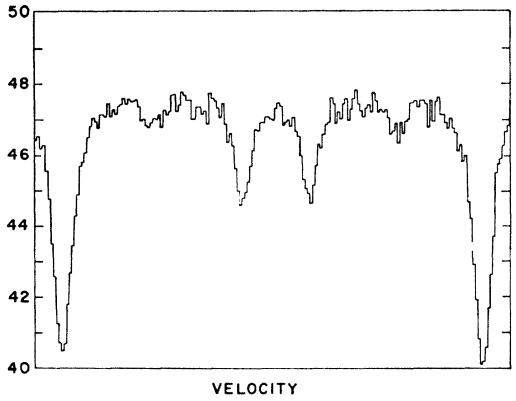

FIG. 1. Mössbauer spectrum of a single crystal of cobalt plated with Co^{57} viewed close to the c axis. The weakness of the $\Delta m=0$ transition confirms that the deposited Co^{57} is epitaxial with the single-crystal substrate. The ordinate is in units of thousands of counts per channel.

or else perpendicular to the gamma ray observation direction, there should be a striking change in the hyperfine pattern, corresponding to the vanishing of the $\Delta m=0$ intensity along the field direction. This is demonstrated in Fig. 1 taken with the crystal plane at 7° to the observation direction. Analysis shows that not more than 15% of the activity may be considered to be improperly sited. An additional test of the epitaxiality is displayed by the behavior of the quadrupole energies as the external field is altered from parallel to perpendicular to the c axis (see Sec. 3). This also confirms that when the field is applied perpendicular to the c axis that the magnetization is turned into the basal plane.

The apparatus is shown schematically in Fig. 2. To the left is the magnet containing the crystal source. The gamma radiation from it passes through an absorber containing sodium ferrocyanide made with enriched Fe^{57} and thence to an NaI scintillation counter. The absorber is constrained to move perpendicular to the sample by balls rolling in precision grooves (i.e., parallel to the bottom of the page). The motion is

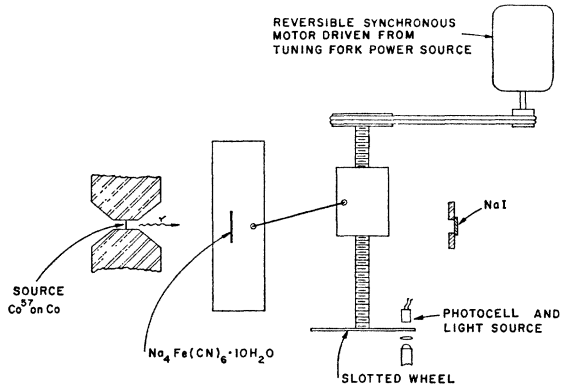

FIG. 2. Schematic diagram of the apparatus and experimental setup.

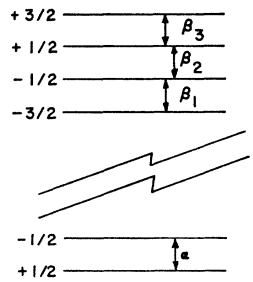

FIG. 3. Energy-level diagram of Fe^{57} in hexagonal cobalt.

obtained from a simple but precision linkage which connects the table to a carriage moving on the lead-screw. The carriage moves to and fro at a constant speed, being driven via pulleys and O-ring belts from a synchronous motor. The latter obtains its power from an amplified voltage derived from a tuning fork oscillator. The detected gamma rays are selected in a single-channel analyzer and stored in a pulse-height analyzer operated in the "time" or multiple scaler mode. The storage channel is advanced by photoelectric signals derived from the passage of light through slots equally spaced on a disc which turns with the screw. The analyzer spends equal time counting in each channel. The velocity of the absorber is given by

$$v=s\frac{\dot{s}}{L(1-s^2/L^2)^{1/2}}=(s\dot{s}/L)\{1+\tfrac{1}{2}(s^2/L^2)+\cdots\},$$

where L is the length of the linkage and s the displacement of the carriage along the screw, measured from the center line. The velocity scale is seen to be nearly a linear function of the displacement s and hence of the channel number. The correction in curly brackets amounts to about 2% at the ends of the screw, and in any case is made precisely. The instrument is calibrated by a measurement of L and $\dot{s}$. The latter is done by connecting a tuning-fork pulser in place of the gamma-ray source.

3. METHOD AND RESULTS

The Fe^{57} nuclear states are split by the magnetic and electric-quadrupole coupling according to the Hamil-

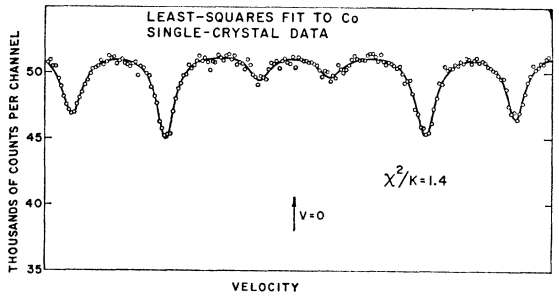

FIG. 4. A typical velocity spectrum. Source: Co^{57} in hexagonal cobalt magnetized parallel to the c axis and perpendicular to the direction of observation of γ radiation. Absorber: sodium ferrocyanide.

TABLE I. Energy splittings for Fe^{57} in cobalt. Symbols are defined in Fig. 3.

H_{ext}(kG)	Orientation	No. of runs	T(°K)	α	β_1	β_2	β_3
0		9	299±2	3.7604 ±0.0022	2.1765 ±0.0022	2.1467 ±0.0022	2.1110 ±0.0022
20.0±0.1	∥ to c	5	299±2	3.5238 ±0.0038	2.0471 ±0.0037	2.0236 ±0.0037	1.9871 ±0.0035
20.0±0.1	⊥ to c	5	299±2	3.5200 ±0.0039	1.9978 ±0.0043	2.0057 ±0.0037	2.0307 ±0.0040
0			77	3.8386 ±0.0030	2.2337 ±0.0028	2.1917 ±0.0031	2.1625 ±0.0027

tonian

$$\mathcal{H}=(\mu_n/I)H_\zeta I_\zeta+\frac{3e^2Q}{4I(2I-1)}V_{\zeta\zeta}[I_\zeta^2-\tfrac{1}{3}I(I+1)], \quad (3.1)$$

where μ_n and Q are the nuclear magnetic and quadrupole moments ($Q=0$ for the ground state), ζ is the direction of alignment of the spins and $\mathbf{H}=\mathbf{H}_n+\mathbf{H}_{ext}$ is the total field acting on the nucleus and is the sum of the hyperfine field H_n and the applied external field H_{ext}. $V_{\zeta\zeta}$ is the component of the electric-field-gradient tensor in the direction ζ. We neglect terms which give second order effects, i.e., $\sim(V_{\zeta\zeta})^2/H_\zeta$.

In zero field or when the field is applied along the c axis $V_{zz}=q$, the principle value of the field-gradient tensor. When the spins are aligned in the basal plane the field gradient is $V_{xx}=V_{yy}=-\frac{1}{2}q$, since there is axial symmetry and by Laplace's theorem $V_{xx}+V_{yy}+V_{zz}=0$. If the components of the hyperfine field in the two directions are $H_{\parallel}$ and $H_\perp$ the energy level diagram is as shown in Fig. 3, with, for the magnetic moment parallel to the z axis

$$\begin{aligned}\beta_3&=\tfrac{2}{3}\mu^*(H_{\parallel}-H_{ext})+\tfrac{1}{2}e^2Qq,\\ \beta_2&=\tfrac{2}{3}\mu^*(H_{\parallel}-H_{ext}),\\ \beta_1&=\tfrac{2}{3}\mu^*(H_{\parallel}-H_{ext})-\tfrac{1}{2}e^2Qq,\\ \alpha&=2\mu(H_{\parallel}-H_{ext}).\end{aligned} \quad (3.2)$$

When the magnetic moment is perpendicular to the z axis

$$\begin{aligned}\beta_3&=\tfrac{2}{3}\mu^*(H_\perp-H_{ext})-\tfrac{1}{4}e^2Qq,\\ \beta_2&=\tfrac{2}{3}\mu^*(H_\perp-H_{ext}),\\ \beta_1&=\tfrac{2}{3}\mu^*(H_\perp-H_{ext})+\tfrac{1}{4}e^2Qq,\\ \alpha&=2\mu(H_\perp-H_{ext}).\end{aligned} \quad (3.3)$$

Here μ and μ^* are the ground- and excited-state magnetic moments, and their spins are $\frac{1}{2}$ and $\frac{3}{2}$, respectively.

A typical run is shown in Fig. 4. The spectra were fitted by a least-squares computer program to a sum of Lorentzians. The results for the energy splittings are summarized in Table I (in units of mm/sec).

Note that the quadrupole splitting changes sign and halves its value when the field is applied perpendicular to c. This confirms that the magnetization must be saturated along the field direction.

The quadrupole coupling e^2Qq may be determined immediately from any set of values for β_1, β_2, and β_3. We find the results shown in Table II, where we have taken the gamma ray energy to be $E=14.37\pm0.01$ keV.[7]

The negative sign for the quadrupole splitting indicates that the quadrupole interaction lowers the energy of the $m=\pm\frac{3}{2}$ states and raises that of the $\pm\frac{1}{2}$ states. The room temperature values are consistent with one another within experimental error. The relative values at room temperature and 77°K are given by

$$(q_{77}-q_{299})/q_{299}=0.09\pm0.09,$$

i.e., they do not differ outside the experimental error. The mean value of $e^2Qq/2$ is -0.032 mm/sec and hence the coupling parameter $e^2Qq=-0.064$ mm/sec.

The magnetic-field measurements can be interpreted using the known[8] value of

$$\mu=0.0903\pm0.0007 \text{ nm}.$$

The excited-state moment we obtain from the relation $\mu^*/\mu=-(\beta_1+\beta_2+\beta_3)/\alpha$. We deduce the values shown in columns 5 and 6 of Table II. The mean value for μ^*/μ was 1.7135 ± 0.0015.

The absolute errors quoted for H_n-H_{ext} are largely

TABLE II. Quadrupole splitting for Fe^{57} in cobalt, assuming $E_\gamma=14.37\pm0.01$ keV.

H_{ext} (kG)	Orientation	T (°K)	$e^2Qq/2$ (mm/sec)	H_n-H_{ext} (kG)	μ^*/μ
0		299	−0.0328±0.0016	−316.6 ±2.5	1.7110 ±0.0020
20.0	∥ to c	299	−0.0300±0.0025	−296.7 ±2.3	1.7191 ±0.0047
20.0	⊥ to c	299	−0.0329±0.0060	−296.4 ±2.3	1.7143 ±0.0054
0		77	−0.0356±0.0039	−323.2 ±2.5	1.7170 ±0.0033

[7] J. B. Bellicard and A. Moussa, J. Phys. Radium **18**, 115 (1957).
[8] G. W. Ludwig and H. H. Woodbury, Phys. Rev. **117**, 1286 (1960).

due to the uncertainty in μ and are therefore not independent. We find

$$H(H_{\rm ext}=0)-H(H_{\rm ext}\|c)=-19.92\pm0.36\ {\rm kG},$$
$$H(H_{\rm ext}=0)-H(H_{\rm ext}\perp c)=-20.24\pm0.37\ {\rm kG},$$

and

$$H_{\|}-H_{\perp}=-0.32\pm0.51\ {\rm kG}$$

at 299°K. We notice that the external field is additive within the accuracy to which $H_{\rm ext}$ is known, and that the hyperfine field parallel and perpendicular to the c axis are equal within the error of 500 G. The value of the hyperfine field at room temperature is -316.6 ± 2.5 kG and varies with temperature as follows:

$$|H_n^{77}|-|H_n^{299}|=6.6\pm0.3\ {\rm kG}.$$

4. INTERPRETATION

Electric-Field Gradient

The electric-field gradient q at the nucleus is the sum of two terms:

$$q=q_{\rm atom}+q_{\rm lattice}$$
$$=-(1-R)\left\langle\sum_e\frac{3\cos^2\theta-1}{r^3}\right\rangle+(1-\gamma_\infty)Z\sum_i\frac{3\cos^2\theta_i-1}{r_i^3}. \quad (4.1)$$

The first term is derived from the electric potential produced by electrons inside the Fe^{57} cell and the summation is taken over these electrons. The second term arises from the potential produced by the ions and electrons outside the cell. The factors $(1-R)$ and $(1-\gamma_\infty)$ represent the effects of the screening or antiscreening of the nucleus by the closed shells of inner electrons.[9] The second summation in Eq. (4.1) has been performed by de Wette[10] using a model with a charge of Z per ion and Z electrons distributed uniformly throughout the cell. For cobalt $Z\sim0.7$ and using the appropriate value $c/a=1.6322$ de Wette's calculation gives the result $q_{\rm lattice}=0.005\times10^{23}(1-\gamma_\infty)$. This is so small and of the opposite sign relative to the observed q of -1.8×10^{23} (which we deduce assuming that $\langle r^{-3}\rangle_{3d}=5.1$ atomic units[11] and $R=0.3$ [12]) that we conclude that we can ignore the lattice term and take q to measure directly the electron asymmetry in the parent cell. [Note that Eq. (4.2) implies that the two contributions will differ in sign.] This contribution is dominated by the $3d$ electrons since they are close to the nucleus. Because q would vanish if the $3d$ band were completely full we may write

$$q=(1-R)\left\langle\sum_h\frac{3\cos^2\theta-1}{r^3}\right\rangle, \quad (4.2)$$

where the sum is now over the holes in the $3d$ band.

For iron in cobalt there are about 2.8 holes[13] and if we assume that R and $\langle r^{-3}\rangle_{3d}$ in the metal are similar to those in the Fe^{++} ion we get

$$\langle3\cos^2\theta-1\rangle_{\rm av}=-0.0019 \quad (4.3)$$

at 299°K and the same within experimental error at 77°K. Here the subscript "av" means "average over the holes in the $3d$ band." This asymmetry is very small. For comparison the largest value possible for $\langle3\cos^2\theta-1\rangle_{\rm av}$ is 4/7 for a single hole in the $3z^2$-r^2 orbital. To a high accuracy therefore the charge density of the $3d$ electrons is unaffected by the hexagonal symmetry.

Hyperfine Field

The hyperfine field in a noncubic substance will show an anisotropy arising from the following contributions: (1) the dipolar field H_d due to the spin moment of the $3d$ electrons; (2) the field H_L due to the orbital moment of the $3d$ electrons; and (3) the field H_s produced by the contact interaction of the s electrons which are polarized by the $3d$ electrons.

On the conventional band model of a metal the charge and spin asymmetries are both due to holes in the $3d$ band, and so the electric field gradient and the dipolar field are proportional to each other. This simple model is not exactly correct because, as Freeman and Watson[12] have shown, spin-polarization effects may give charge and spin distributions of different shapes. The dipolar contribution to the hyperfine field is

$$\mathbf{H}_d=-2\mu\langle\sum_e\{3(\mathbf{s}\cdot\mathbf{r})\mathbf{r}-\mathbf{s}r^2\}/r^5\rangle, \quad (4.4)$$

where μ is the Bohr magneton. With the magnetization along the c axis this is, for the simple model,

$$\begin{aligned}H_d&=2\mu\langle\sum_h s(3\cos^2\theta-1)/r^3\rangle\\&=-\mu\langle2s\rangle\langle(3\cos^2\theta-1)/r^3\rangle_{\rm av}\\&=\mu n_h\langle(3\cos^2\theta-1)\rangle_{\rm av}\langle r^{-3}\rangle_{3d}\\&=\mu q,\end{aligned} \quad (4.5)$$

where n_h is the number of holes.
From the observed value of q we therefore expect

$$H_d=-1.8\ {\rm kG}, \quad (4.6)$$

which is small compared with the total hyperfine field of 316.6 kG. When the external field is applied perpendicular to the c axis the dipolar contribution changes

[9] R. Sternheimer, Phys. Rev. **84**, 244 (1951); **95**, 736 (1954); **105**, 158 (1957).
[10] F. W. de Wette, Phys. Rev. **123**, 103 (1961).
[11] Abragam and Boutron, Compt. Rend. **252**, 2404 (1961).
[12] A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963).
[13] M. F. Collins and J. B. Forsyth, Phil. Mag. **8**, 401 (1963).

from H_d to $-H_d/2$. We therefore expect a contribution of about -2.7 kG to $H_{\parallel}-H_{\perp}$ but experimentally $H_{\parallel}-H_{\perp}$ is zero within the experimental error. Some additional contribution of opposite sign is therefore required for $H_{\parallel}-H_{\perp}$ if we continue to use the simple model.

Another orientation-dependent term is the field due to the orbital current. It may be written as

$$H_L=\mu n_h\langle r^{-3}\rangle_{3d}(g-2), \tag{4.7}$$

and Marshall has estimated it to be of the order of $+50$ kG in cobalt. It will be anisotropic since g is anisotropic and the contribution to $H_{\parallel}-H_{\perp}$ is

$$\Delta H_L=\mu n_h\langle r^{-3}\rangle_{3d}(g_{\parallel}-g_{\perp}). \tag{4.8}$$

We also expect the bulk of the hyperfine interaction H_s arising from the contact interaction of the s electrons to depend upon spin orientation, and we can give a rough estimate of the order of magnitude of the effect as follows. From experiment H_s is of the order of -400 kG. Because of spin-orbit interaction the various $3d$ states are mixed and we expect a difference of the order of $H_s(g-2)^2$ between the field in a real metal and that for a hypothetical metal with zero spin-orbit coupling. Hence we expect a contribution to ΔH of

$$\Delta H_s\simeq H_s(g_{\parallel}+g_{\perp}-4)(g_{\parallel}-g_{\perp}). \tag{4.9}$$

With $g_{\parallel}-2\simeq g-2\simeq 0.1$ we find (4.9) to be an order of magnitude smaller than (4.8). We therefore assume ΔH_s may be neglected.

Summing the contributions to the anisotropy we have

$$\begin{aligned}\Delta H&=\Delta H_d+\Delta H_L\\&=\tfrac{3}{2}H_d+\mu n_h\langle r^{-3}\rangle_{3d}(g_{\parallel}-g_{\perp}).\end{aligned} \tag{4.10}$$

Equating ΔH to zero and using (4.6) we arrive at the result

$$g_{\parallel}-g_{\perp}\simeq+0.003. \tag{4.11}$$

We should emphasize that we regard this last result as very tentative in view of the chain of assumptions we have made in deducing it. We believe it is particularly unsatisfactory to have to postulate an accidental cancellation between the dipolar and orbital terms as an explanation of the observed zero value of ΔH. A possible alternative to this explanation is to assume that because of spin polarization effects the asymmetry of the spin density is not simply related to the charge density.

5. DISCUSSION

Our results show that the asymmetry of the charge distribution on an iron atom in hexagonal cobalt is

$$\langle 3\cos^2\theta-1\rangle_{\text{charge}}=-0.0019. \tag{5.1}$$

While there are no other relevant data on iron in cobalt it is interesting to compare this figure with measurements on pure cobalt. No quadrupole splitting has been detected in the NMR in hexagonal cobalt, but data which are sensitive to the symmetry of the spin density is available from neutron diffraction and from NMR.

Moon[14] has measured the scattering of polarized neutrons from a cobalt single crystal and from the asphericity of the form factor he deduced that the magnetic moment density has the form

$$\begin{aligned}|u(\theta)|^2=0.394|u_{xy,x^2-y^2}|^2+0.416|u_{yz,zx}|^2\\+0.190|u_{3z^2-r^2}|^2,\end{aligned} \tag{5.2}$$

where $|u_{xy,x^2-y^2}|^2$ is the spin density distribution for the orbitals xy and x^2-y^2 etc. (For spherical symmetry the coefficients of the $|u|^2$'s would be 0.4, 0.4 and 0.2, respectively). This gives for the asymmetry of the spin density

$$\langle 3\cos^2-1\rangle_{\text{spin}}=0.0023. \tag{5.3}$$

Although this is not directly comparable with our results it is satisfying that the asymmetries are of the same order of magnitude although the sign difference is perhaps surprising. Taking $n_h=1.7$ for cobalt the dipolar field turns out to be $+1.5$ kG.

Koi, Tsujimura, Hihara, and Kushida[4] have made NMR measurements on both cubic and hexagonal cobalt as a function of temperature. They find that $|H_n|$ is greater in the hexagonal phase by about 11 kG at low temperatures and this difference decreases with increasing temperature to an almost constant value of 3.5 kG in the region of the hcp $\rightarrow$ fcc transition point of 723°K. Keffer and Portis[15] suggested that the c/a ratio becomes close to ideal in this region so that the dipolar field is small and the residual difference is due to an intrinsic difference between the phases, e.g., in atomic volume, and the extra 7.5 kG at low temperatures is the true dipolar field. However, the neutron-scattering and Mössbauer effect results suggest that even this difference is too large to be accounted for by dipolar effects.

We conclude that the details of the hyperfine interaction in metals are still imperfectly understood. Further systematic measurements on noncubic metals and alloys should prove a valuable means of studying the electronic structure of atoms in the metallic state.

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[14] R. M. Moon, Phys. Rev. **136**, A195 (1964).
[15] Quoted in Ref. 4.