Indirect Exchange Coupling of Nuclear Magnetic Moments by Conduction Electrons*

M. A. RUDERMAN AND C. KITTEL
Department of Physics, University of California, Berkeley, California
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A calculation is given of the indirect exchange $\mathbf{I}_i \cdot \mathbf{I}_j$ type coupling of nuclear magnetic moments in a metal by means of the hyperfine interaction with the conduction electrons. The interaction appears to account qualitatively for the broad nuclear spin resonance lines observed in natural metallic silver. It is expected that the interaction may sharpen the resonances in pure isotopic specimens. The line shape of the minority isotope in a binary mixture may tend to be Gaussian, while that of the majority isotope may tend to be Lorentzian, if the indirect exchange interaction is dominant.

INTRODUCTION

SEVERAL recent measurements suggest that the width of nuclear-spin resonance lines in the heavier metals may be greater than expected from magnetic dipolar interactions alone. The additional broadening for nuclei with spin $I>\frac{1}{2}$ might be caused in part by the interaction of the nuclear electric quadrupole moment with lattice imperfections, but nuclei with $I=\frac{1}{2}$ have zero quadrupole moment, so that here other broadening mechanisms must be effective. Among nuclei with $I=\frac{1}{2}$, Bloembergen and Rowland[1] report anomalous line widths in tin and thallium; the widths are of the order of five times the calculated dipolar widths. Sogo and Jeffries[2] find that the width peak-to-peak of the absorption derivative of the Ag^{109} resonance in natural silver is approximately 115 ± 15 cps, whereas the corresponding calculated dipolar width is only about 50 cps. While some of the examples might be explained by spin-lattice relaxation or the possible presence of paramagnetic impurities, we would like to suggest a more general mechanism.

There will exist in metals a coupling between the magnetic moments of two nuclei *via* their hyperfine interaction with the conduction electrons. Ramsey and others[3] have shown that a similar interaction exists between nuclear spins in molecules. Let us consider a metal crystal in which all but two of the nucleons are nonmagnetic. The electron wave functions of the perfectly periodic problem will be scattered by the hyperfine interaction with each of the magnetic nucleons. The total wave function seen by one magnetic nucleon will depend on the spin orientation of the other, thus establishing an indirect spin-dependent coupling between the two nucleons. We proceed to calculate the interaction by second-order perturbation theory. The interaction will be shown to have the form $\mathbf{I}_i \cdot \mathbf{I}_j$ of an exchange operator, suggesting that the interaction may sharpen[4] the line in pure isotopic specimens, while broadening the line in isotopic mixtures. The observed line width in natural silver appears to be in qualitative agreement with our calculations. We assume throughout that the contact part of the hyperfine interaction is dominant, and that the dipolar part of this interaction may be neglected.

CALCULATION

We consider first an electron moving in an exactly periodic lattice; interactions with nuclear spins and lattice vibrations are neglected. The electron can be described by the Bloch function $\phi_{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is periodic in the lattice. It is convenient to normalize ϕ so that for large volumes,

$$V^{-1}\int\int\int d\tau\phi_{\mathbf{k}}{}^*\phi_{\mathbf{k}}\rightarrow 1. \tag{1}$$

The interaction between nuclear and electron spins is manifest in hyperfine structure. This same interaction will of course couple Bloch functions of different $\mathbf{k}$, i.e., scatter conduction electrons. The matrix element for the scattering from $\mathbf{k}$ to $\mathbf{k}'$ by the moment μ on the nucleus at $\mathbf{r}=\mathbf{R}_i$ is

$$\mathbf{S}\cdot\mathbf{I}_i\Delta_{\mathbf{k}\mathbf{k}'}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_i}, \tag{2a}$$

$$\Delta_{\mathbf{k}\mathbf{k}'}\equiv\int\int\int d\tau\phi_{\mathbf{k}'}{}^*(\mathbf{r})\Delta\phi_{\mathbf{k}}(\mathbf{r})=\Delta_{\mathbf{k}'\mathbf{k}}{}^*. \tag{2b}$$

Here $\mathbf{S}$ and $\mathbf{I}$ are the spin operators for the electron and nucleus; Δ is the hyperfine interaction. Since the interaction (2) is so weak compared to the electron-lattice coupling it is sufficient to treat it as a small perturbation. We assume the conduction band is filled in both spin states from $k=0$ to k_m. Then the interaction between the spins of nuclei i and j at $\mathbf{r}=\mathbf{R}_i$ and $\mathbf{R}_j$, via the double scattering of an electron $(\mathbf{k}\rightarrow\mathbf{k}'\rightarrow\mathbf{k})$, is

$$H(\mathbf{R}_{ij})=-(\mathbf{S}\cdot\mathbf{I}_i)(\mathbf{S}\cdot\mathbf{I}_j)\int_0^{k_m}\frac{d\mathbf{k}}{(2\pi)^3}\times\int_{k_m}^{\infty}\frac{d\mathbf{k}'}{(2\pi)^3}\frac{\Delta_{\mathbf{k}\mathbf{k}'}\Delta_{\mathbf{k}'\mathbf{k}}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}}}{E(\mathbf{k}')-E(\mathbf{k})}+\text{c.c.} \tag{3}$$

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[1] N. Bloembergen and T. J. Rowland, Acta Metallurgica **1**, 731 (1953).

[2] P. B. Sogo and C. D. Jeffries (private communication) the shape is approximately Gaussian.

[3] N. F. Ramsey, Phys. Rev. **91**, 303 (1953); N. F. Ramsey and E. M. Purcell, Phys. Rev. **85**, 143 (1952); E. L. Hahn and D. E. Maxwell, Phys. Rev. **88**, 1070 (1952); also work by Gutowsky, McCall, and Slichter, Phys. Rev. **84**, 589 (1951).

[4] C. J. Gorter and J. H. Van Vleck, Phys. Rev. **72**, 1128 (1947).

The restriction $k'>k_m$ is dictated by the exclusion principle. However, it will be evident that the exclusion principle can be neglected in the intermediate states k'.

The hyperfine interaction does not depend strongly on k. Since the largest contributions to Eq. (3) come when $k'\sim k\sim k_m$, we approximate

$$\Delta_{\mathbf{k}\mathbf{k}'}\Delta_{\mathbf{k}'\mathbf{k}} \quad \text{by} \quad |\Delta_{k_m k_m}|^2.$$

Summing over the electron spins and performing all angular integrations we obtain for (3):

$$\frac{\mathbf{I}_i\cdot\mathbf{I}_j|\Delta_{k_m k_m}|^2}{(2\pi)^4 R_{ij}^2}\int_{-k_m}^{k_m} kdke^{ikR_{ij}} \times\left[\int_{k_m}^{\infty}+\int_{-\infty}^{-k_m}\frac{e^{ik'R_{ij}}k'dk'}{E(k')-E(k)}\right]. \quad (4)$$

In deriving (4) it has been assumed that $E(k)$ depends only upon the magnitude of k.

It is perhaps of some interest to show how the exclusion principle plays no real role in the k' integration. The bracket in (4) may be written:

$$\text{P.P.}\left[\int_{-\infty}^{\infty}\frac{e^{ik'R}k'dk'}{E(k')-E(k)}-\int_{-k_m}^{k_m}\frac{e^{ik'R}k'dk'}{E(k')-E(k)}\right]. \quad (5)$$

Putting the second integral of (5) into (4), we have a constant times

$$\text{P.P.}\int_{-k_m}^{k_m}dk\int_{-k_m}^{k_m}dk'e^{i(k+k')R}kk'[E(k')-E(k)]^{-1}. \quad (6)$$

Expression (6) vanishes because the integrand is antisymmetric in k and k'. Therefore we may replace the bracket in (4) by the first integral of (5) which is the result which would have obtained if the exclusion principle had been neglected in intermediate states in (3). This, of course, must be quite generally true since the conduction band could have been "filled" before or after introducing the perturbation (3).

If it is assumed that the effective mass does not vary appreciably for k in the neighborhood of k_m we may put $E(k)=\hbar^2k^2/2m^*$. Then (4) becomes

$$\frac{\mathbf{I}_i\cdot\mathbf{I}_j}{4}\frac{|\Delta_{k_m k_m}|^2 m^*}{(2\pi)^3 R_{ij}^4\hbar^2}[2k_mR_{ij}\cos(2k_mR_{ij})-\sin(2k_mR_{ij})]. \quad (7)$$

The quantity $\Delta_{k_m k_m}$ can be simply related to the observed atomic hyperfine structure splitting ν_a. From Eqs. (1) and (2) the hyperfine splitting for a conduction electron with wave number k is given by

$$[(2I+1)/2\Omega]\Delta_{kk}=2\pi\hbar\nu_{\text{hfs}}(k). \quad (8)$$

Ω is the atomic volume which enters because of the normalization (1). The observed hyperfine interaction in the free atom and crystal are comparable, differing because of the changed electron density in the vicinity of $r=0$, i.e.,

$$\nu_{\text{hfs}}(k)/\nu_a\approx\Omega^{-1}\phi_k^2(0)/\psi^2(0)\equiv\xi; \quad (9)$$

ξ is generally less than but of order one.

APPLICATIONS

We see that the interaction energy between nucleon spins in a metal is of the form

$$\mathcal{H}=\sum_{i>j}\sum_j A_{ij}\mathbf{I}_i\cdot\mathbf{I}_j, \quad (10)$$

where

$$A_{ij}=\frac{\Omega^2 m^*\xi_i\nu_a(i)\xi_j\nu_a(j)}{2\pi(2I_i+1)(2I_j+1)}\left(\frac{1}{R_{ij}}\right)^4 \times[2k_mR_{ij}\cos(2k_mR_{ij})-\sin(2k_mR_{ij})]. \quad (11)$$

This interaction is in addition to the usual dipolar and quadrupolar interactions. We note that A_{ij} depends on the product $\mu_i\mu_j$ of the nucleon magnetic moments. A qualitative estimate suggests that the new interaction will be of the same order of magnitude as the magnetic dipolar interaction when the electron density at the nucleon in the metal is of the order of a few hundred times greater than the density of a uniform distribution of charge, as in a plane wave. Using atomic hyperfine separations (with $\xi=1$), we estimate the following density ratios:

Li	Na	K	Ag	Rb	Cs
35	200	550	1100	1600	3100

We now consider the effect of a strong $\mathbf{I}_i\cdot\mathbf{I}_j$ interaction on the width and shape of nuclear resonance lines. That the interaction is of the form Eq. (10) follows from the matrix element (2) and is independent of any of the subsequent approximations. This interaction is of the same type as the electron exchange interaction $\mathbf{S}_i\cdot\mathbf{S}_j$, of which the properties with respect to electron resonance experiments have been studied in particular detail by Van Vleck,[5] whose results we use here. In a metal consisting entirely of one isotope the nuclear exchange interaction tends to sharpen the resonance line. The second moment $\langle(\Delta\nu)^2\rangle$ is not affected by the exchange interaction, while the fourth moment $\langle(\Delta\nu)^4\rangle$ is increased. As the line sharpens the shape is said approximately to go from Gaussian to Lorentzian. We have been unable to find accounts of nuclear resonance experiments in metals carried out under conditions which would provide a critical test of the predicted sharpening, although the corresponding effect is well known in electron spin resonance. When the line width is reduced, the reduction is roughly in the ratio of the dipolar interaction to the exchange interaction.†

[5] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948); see also P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953).

† *Note added in proof.*—In a private communication N. Bloembergen reports that he has observed effects of this nature in

An interesting situation arises when the crystal consists of two magnetic ingredients with gyromagnetic factors sufficiently different that the resonances for the two varieties of nuclei do not overlap. Here the nuclear exchange interaction between unlike nucleons tends to broaden each resonance line. We shall apply the results of Van Vleck to the nuclear resonance in natural silver, which consists of roughly equal parts Ag^{107} and Ag^{109}, both isotopes having $I=\frac{1}{2}$. The nuclear magnetic moments are[6]

$$\mu_{107}=-0.113 \text{ nm},$$

$$\mu_{109}=-0.130 \text{ nm};$$

the atomic ground-state hyperfine splittings are[7]

$$\nu_{107}=1713 \text{ Mc/sec},$$

$$\nu_{109}=1977 \text{ Mc/sec}.$$

The expression for $\langle(\Delta\nu)^4\rangle$, Van Vleck's Equation (29), is formidable. We shall evaluate it approximately for silver under three simplifying assumptions: (a) the dipolar interaction is neglected; (b) only nearest neighbor exchange interactions are considered; (c) all nearest neighbor nuclear exchange interactions are taken to be equal, independent of the isotopes involved. Thus $A_{jk}=A_{jk'}=A_{j'k}=A_{j'k'}=A$, for nearest neighbors, where the sites j, k may be occupied by primed or unprimed nuclear varieties.

We consider the moments of the resonance line of the unprimed nucleons, with $I=I'=\frac{1}{2}$. From Van Vleck's Equation (28),

$$h^2\langle(\Delta\nu)^2\rangle=(4N)^{-1}\sum_j\sum_{k'}A_{jk'}^2, \tag{12}$$

where N is the number of unprimed nucleons in the specimen. We calculate for a face-centered cubic lattice, for which each site has 12 nearest neighbor sites. We let f be the fraction of sites occupied by the primed variety and $(1-f)$ the fraction of sites occupied by the unprimed variety, the two varieties being distributed entirely at random. It is readily seen that the value of the double summation is $12NfA^2$, so that

$$h^2\langle(\Delta\nu)^2\rangle=3fA^2. \tag{13}$$

We have for the fourth moment, from Van Vleck's Equation (29), letting Σ' denote a sum over indices larger than those in the preceding summation,

$$\begin{aligned}h^4\langle(\Delta\nu)^4\rangle=&(8N)^{-1}\sum_{l'}\sum_j\sum_k{}'A_{jk}^2(A_{jl'}^2+A_{kl'}^2\\&-2A_{jl'}A_{kl'})+(8N)^{-1}\sum_j\sum_{k'}\sum_{l'}{}'\\&\times[A_{k'l'}^2(A_{jk'}^2+A_{jl'}^2-2A_{jk'}A_{jl'})\\&+3A_{jk'}^2A_{jl'}^2]+(16N)^{-1}\sum_j\sum_{k'}A_{jk'}^4.\end{aligned} \tag{14}$$

We discuss on the foregoing assumptions the several summations, letting $\sum$ denote the appropriate multiple summation:

$$\begin{aligned}&\sum A_{jk}^2A_{jl'}^2=\sum A_{jk}^2A_{kl'}^2=66N(f-f^2)A^4;\\&\sum A_{jk}^2A_{jl'}A_{kl'}=24N(f-f^2)A^4;\\&\sum A_{k'l'}^2A_{jk'}^2=\sum A_{k'l'}^2A_{jl'}^2=66Nf^2A^4;\\&\sum A_{k'l'}^2A_{jk'}A_{jl'}=24Nf^2A^4;\\&\sum A_{jk'}^2A_{jl'}^2=66Nf^2A^4;\\&\sum A_{jk'}^4=12fNA^4.\end{aligned} \tag{15}$$

We have then

$$h^4\langle(\Delta\nu)^4\rangle=(9/4)(5f+11f^2)A^4. \tag{16}$$

For equal proportions of the two varieties, as is approximately true of natural silver, $h^4\langle(\Delta\nu)^4\rangle=11.8A^4$, while $h^2\langle(\Delta\nu)^2\rangle=1.5A^2$. We have

$$\langle(\Delta\nu)^4\rangle^{\frac{1}{4}}/\langle(\Delta\nu)^2\rangle^{\frac{1}{2}}=1.51,$$

while with a Gaussian distribution the ratio would be 1.32. For small f the fourth moment tends to dominate the square of the second moment, and the line may approach an approximate Lorentzian distribution, just as in the dilution problem considered earlier.[8]

We now estimate the nearest neighbor nuclear exchange constant A for silver, taking $m^*=1$ and $\xi=1$. We find $A\cong2.5\times10^{-25}$ erg or $A/h\cong40$ cps. The rms width in natural silver from nearest neighbor exchange interactions alone is then 50 cps. This may be increased by about 20 percent when the exchange type interactions of more distant neighbors is taken into account. This estimated rms exchange width of $\sim$60 cps is to be compared with a calculated rms width from the dipolar interaction of order 25 cps; the dipolar interaction will increase the over-all calculated width slightly. Taking the line shape to be Gaussian, as is observed, the experimental rms value is $\Delta\nu=55\pm8$ cps.[9] Of course any agreement would be certainly accidental; it is not necessarily true that $m=m^*$ and $\xi=1$. Interpretation of the Knight shift[10] in silver on the assumption $m^*=m$ leads to the value $\xi\cong0.7$. An estimate of the spin-lattice relaxation time using the observed Knight shift and the Korringa[11] relation leads to $T_1\cong0.02$ sec, so that this might contribute $\sim$10 cps to the width. It appears that our interpretation of the silver line width would lead to ξ near 0.8.

If the nuclear spins are aligned the energy levels of the conduction electrons are split by the hyperfine interaction: those electrons whose moment is parallel to the nuclear magnetization have their energy lowered by $I\Delta(2\Omega)^{-1}$. This is of order kT for temperatures around

thallium metal specimens as the isotope ratio Tl^{205}/Tl^{203} is varied. He suggests that the dipolar part of the hyperfine interaction may make a contribution here.

[6] Brun, Oeser, Staub, and Telschow, Phys. Rev. **93**, 172 (1954).

[7] G. Wessel and H. Lew, Phys. Rev. **91**, 476 (1953).

[8] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).

[9] For a Gaussian, the rms width is one-half of the peak-to-peak absorption deviation.

[10] P. B. Sogo and C. D. Jeffries, Phys. Rev. **93**, 174 (1954).

[11] J. Korringa, Physica **16**, 601 (1950).

10^{-6} °K. Fröhlich and Nabarro[12] have investigated the behavior of the nuclear and electron spin systems below these temperatures including the slight change in population between the two electron spin states but neglecting the interaction Eq. (10). They conclude that below 10^{-6} °K the system of nuclear moments has ferromagnetic behavior. However, we see from Eq. (11) that the inclusion of the exchange interaction (which is essentially independent of the relative population of the electron spin states) makes the situation obscure. For nearest neighbors A_{ij} is positive and therefore gives a higher energy when spins are parallel than when antiparallel. This interaction energy is comparable to that from the Fröhlich-Nabarro effect. The exchange interaction varies at large distance as $R^{-3}\cos(k_mR)$, so that when the nuclear spins are ordered a nearest neighbor approximation is inadequate. We have made no attempt to calculate the nature of the lowest-energy state of the coupled-spin systems.

We are happy to thank E. Teller for contributing a number of pertinent questions and answers. We wish to express our appreciation to W. D. Knight for many helpful discussions of the experimental data. We are grateful to C. D. Jeffries and P. B. Sogo for permission to refer to their unpublished measurements on silver and to N. Bloembergen for communication of his results on metallic thallium. John Walsh has kindly checked our calculations.

[12] H. Fröhlich and F. R. N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940).

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Identification of Gadolinium and Terbium Radioisotopes as Fission Products of U^{235}

E. C. Freiling, L. R. Bunney, and N. E. Ballou
U. S. Naval Radiological Defense Laboratory, San Francisco, California
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The identification of Gd^{159} and Tb^{161} as products of the neutron-induced fission of U^{235} has been confirmed. By a comparison of counting rates with Mo^{99}, the fission yields have been estimated to be 1.1×10^{-3} and 8×10^{-5} percent, respectively.

THE radionuclides, Gd^{159} and Tb^{161}, have been found to be among the products of nuclear fission in numerous cation exchange resin separations[1] of rare earth fission products done over the past year. As expected from an extrapolation of the fission yield curve,[2] the fission yields of these radionuclides are rather low; however, development of quite efficient rare earth separation procedures[1] has made possible the ready identification of them among the other rare earth fission product radionuclides. Described below are summaries of experimental techniques used and preliminary estimates of yields of Gd^{159} and Tb^{161} formed in thermal neutron fission of U^{235}.

TABLE I. Fission yields of Gd^{159} and Tb^{161} relative to Mo^{99}.

Experiment	Fission yields Gd^{159} (in percent $\times10^3$)	Tb^{161} (in percent $\times10^5$)
1*a*	1.02	8.1
1*b*	1.07	(12.8)[a]
2*a*	1.19	7.6
2*b*	1.30	9.3
Average	1.14±0.13[b]	8.3±0.9

[a] Not included in average.
[b] Standard deviation.

[1] E. C. Freiling and L. R. Bunney, J. Am. Chem. Soc. **76**, 1021 (1954).
[2] C. D. Coryell and N. Sugarman, Editors, *Radiochemical Studies: The Fission Products* (McGraw-Hill Book Company, Inc., New York, 1951), National Nuclear Energy Series, Plutonium Project Record, Vol. 9, Div. IV, p. 537.

Samples of both normal uranium and of uranium enriched in U^{235} were rigorously purified of rare earth impurities. (Gadolinium is of major concern here since neutron capture reactions in it lead to formation of the radionuclides being studied.) Purification was based on elution of uranium from a strongly acidic cation exchange resin with 1.0*M* ammonium lactate at *p*H 3.0. The uranium was eluted much ahead of any rare earth impurities.

The highly purified uranium samples were irradiated for one hour in the Materials Testing Reactor,[3] following which radiochemical analyses for rare earth radionuclides and Mo^{99} was performed. In addition to the previously known fission product radionuclides Nd^{147}, Pm^{149}, Sm^{153}, Eu^{156}, and Y^{91}, the radioisotopes of gadolinium and terbium, Gd^{159} and Tb^{161}, were also identified. Estimates of the fission yields of the latter were made by comparisons to Mo^{99}, whose fission yield was taken as 6.2 percent.[2] The values obtained in duplicate determinations on two different irradiated samples of uranium are given in Table I.

The fission yields of Gd^{159} and Tb^{161} lie on a smooth extrapolation of the previously established fission yield curve.[2] Although the standard error is about 10 percent, the absolute accuracy of the indicated fission yields may be no better than about 30 percent. Improvements in the absolute beta-ray counting measurements will materially improve the accuracy.

[3] J. R. Huffman, Nucleonics **12**, No. 4, 21–26 (1954).