The secular determinant is

$$\begin{vmatrix} -\omega & -iG(0) & 0 & D(0) & 0 & C(0) \\ iR(0) & -\omega & -F & 0 & F & 0 \\ 0 & C(k_0) & -\omega & -iG(k_0) & 0 & 0 \\ F & 0 & iR(k_0) & -\omega & 0 & 0 \\ 0 & D(-k_0) & 0 & 0 & -\omega & -iG(k_0) \\ -F & 0 & 0 & 0 & iR(k_0) & -\omega \end{vmatrix} = 0. \tag{A8}$$

We express ω in a series with H as the expansion parameter:

$$\omega = \omega_0 + \omega_1 H + \omega_2 H^2 + \cdots. \tag{A9}$$

For $\omega(0)$, the frequency of interest, $\omega_0 = 0$. It is possible to expand (A8), choose the lowest order terms in H (of order H^2), and set them equal zero. (This corresponds to the usual perturbation method.) This gives a value for $H^2\omega_1^2(0)$,

$$H^2\omega_1^2(0) = R(0)\{G(0) + [1/G(k_0)] \times [D(-k_0)C(0) + D(0)C(k_0)]\}. \tag{A10}$$

Here $R(0)$ and $G(k_0)$ are of the order of H^0, C and D are of order H, and $A(0)$ is of order H^2. The expression in the curly brackets is equal to zero. Thus as noted in Sec. 3.4, $\omega(0)$ is zero to first order in H.

It is interesting to note that this result does not hold true for the case of an antiferromagnet confined to an easy plane with an applied field in the plane perpendicular to the unperturbed position of the spins.[14] For this particular case, k_0 lies at the edge of the Brillouin zone so that $+k_0$ and $-k_0$ are equivalent. This means that $\mathbf{S}(q+k_0)$ is the same as $\mathbf{S}(q-k_0)$. In this case, (A8) reduces to a 4×4 determinant with no elements connecting $q=0$ and $q=k_0$.

$$\begin{vmatrix} -\omega & -iG(0) & 0 & 0 \\ iR(0) & -\omega & 0 & 0 \\ 0 & 0 & -\omega & -iG(k_0) \\ 0 & 0 & iR(k_0) & -\omega \end{vmatrix} = 0 \tag{A11}$$

and

$$H\omega_1 = (G_0 R_0)^{\frac{1}{2}}. \tag{A12}$$

Using (A5a) and (A7a),

$$H\omega_1 = gBH\left[\frac{J(k_0) - J(0) - K(0)}{2J(k_0) - J(2k_0) - J(0)}\right]^{\frac{1}{2}}. \tag{A13}$$

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[14] T. Nagamiya, K. Yosida, and R. Kubo, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

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Nuclear Magnetic Resonance in Metallic Single Crystals

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A method is presented for observing nuclear magnetic resonance absorption in metallic single crystals. Single crystals thick compared to the skin depth are used and accurate corrections are made for the distortion due to eddy currents. Experimental results for aluminum and copper single crystals with the fixed magnetic field parallel to the [001], [$\bar{1}$11], and [$\bar{1}$10] directions, respectively, demonstrate the feasibility of the method. The Knight shifts in aluminum and copper are found to be isotropic and equal to the powder values. The experimental second moments vary with orientation approximately in proportion to the theoretical second moments, but are somewhat larger, as in the powders.

INTRODUCTION

SINCE the discovery of nuclear magnetic resonance absorption (NMR) in metallic copper by Pound,[1] NMR experiments have been performed on a wide variety of metals and alloys. Because of the classical skin effect arising from eddy currents, the radio-frequency magnetic fields will penetrate a good conductor only to a depth of a few thousandths of a centimeter. For this reason, virtually all the NMR work on metals up to now has been performed on finely divided powders, thin polycrystalline foils, or thin evaporated layers. No NMR experiments have been reported on metallic single crystals. It would be highly desirable in studying many phenomena in metals, such as anisotropic Knight shifts and relaxation times or quadrupole interactions, to work with single crystals. The purpose

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[1] R. V. Pound, Phys. Rev. **73**, 1112 (1948).

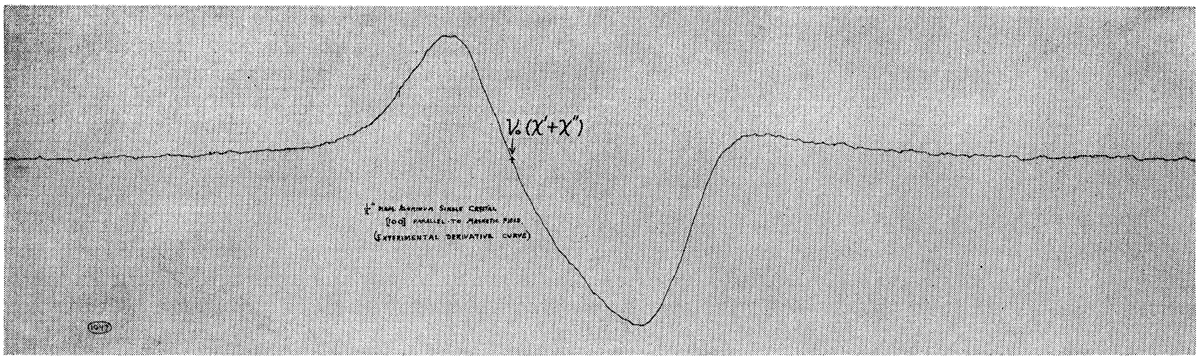

FIG. 1. Spectrometer recording of nuclear resonance absorption derivative in a $\frac{1}{2}$-in. diam, $\frac{3}{4}$-in. long aluminum single crystal for the magnetic field along the [001] direction. $\nu_0(\chi'+\chi'')$ is the "resonant frequency."

of this paper is to point out that, in a number of cases, sufficiently high signal to noise can be obtained from just the surface of a large single crystal and that the distortion in such a signal can be accurately corrected. Experimental results for aluminum and copper single crystals demonstrate the feasibility of this approach. These metals were chosen for the initial experiments because of the relatively high signal to noise obtainable and because their cubic structures give one confidence that the results to be expected from a valid single-crystal experiment can be predicted from the data on powders.[2]

METHOD

For a good conductor of arbitrary thickness it has been shown[3] that due to the skin effect, the nuclear magnetic absorption as measured, for example, with a Pound spectrometer, is proportional to a linear combination, $a\chi'+b\chi''$, of χ', the dispersive part, and χ'', the absorptive part, of the complex nuclear susceptibility. There are two limiting cases of interest[3,4]: (1) For samples with at least one dimension small compared to the skin depth, $a=0$, and the measured absorption is proportional to χ'' alone; and (2) for samples large compared to the skin depth, $a/b=1$, and the measured absorption is proportional to $\chi'+\chi''$. Since the theoretical interpretation of nuclear resonance data usually involves a knowledge of χ'', samples small compared to the skin depth have the obvious advantage of giving χ'' directly, and in addition, can have the advantage of a high filling factor and the resulting higher signal to noise ratio. This is the reason that nearly all NMR experiments on metals have been performed on such samples. It is of interest to note, however, that the first observation[1] of nuclear resonance absorption in a metal was the discovery of the resonance in the copper coil of the rf probe. This corresponds to the second limiting case above.

In order to observe χ'' directly in a metallic single crystal, one needs a crystal with at least one dimension small compared to the skin depth. If a high filling factor is desired, one needs a number of these crystals identically oriented and with faces cut parallel to a high degree of accuracy. Such a sample would be very difficult to fabricate, however, and this is presumably the reason that no nuclear resonance experiments on metallic single crystals have been reported. Based on the observation that for a number of metals, a high filling factor is not necessary, we use single crystals which are very thick compared to the skin depth. With the usual modulation technique, the experimental data will then be of the form

$$f(\nu)=d/d\nu[\chi'(\nu)+\chi''(\nu)],$$

where ν is the frequency. We obtain $\chi''(\nu)$, or $\chi'(\nu)$, from $f(\nu)$ by a theoretical computation. We define

$$g(\nu)\equiv\chi'(\nu)+\chi''(\nu)=\int_0^{\nu}f(\nu')d\nu', \tag{1}$$

which is simply the integral of the experimental curve. Using the appropriate form of the Kramers-Kronig relations,[5] we can write

$$h(\nu)\equiv\chi'(\nu)-\chi''(\nu)=-\frac{1}{\pi}\int_0^{\infty}f(\nu')\ln|\nu'-\nu|d\nu'. \tag{2}$$

Then

$$\chi'(\nu)=\tfrac{1}{2}[g(\nu)+h(\nu)],$$
$$\chi''(\nu)=\tfrac{1}{2}[g(\nu)-h(\nu)].$$

An example of a spectrometer recording of nuclear resonance absorption in a metallic single crystal very thick compared to the skin depth is shown in Fig. 1. This is the expected line shape for $d(\chi'+\chi'')/d\nu$.[3,4] The major peaks are of unequal height, there is an overshoot on the high-frequency side, and both tails are decreasing

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[2] A brief account of this work was presented at the meeting of the American Physical Society, Baltimore, Maryland, March, 1962 [P. L. Sagalyn and J. A. Hofman, Bull. Am. Phys. Soc. **7**, 226 (1962); J. A. Hofmann and P. L. Sagalyn, Bull. Am. Phys. Soc. **7**, 226 (1962)].

[3] A. C. Chapman, P. Rhodes, and E. F. W. Seymour, Proc. Phys. Soc. **70**, 345 (1957).

[4] N. Bloembergen, J. Appl. Phys. **23**, 1383 (1952).

[5] G. E. Pake and E. M. Purcell, Phys. Rev. **74**, 1184 (1948).

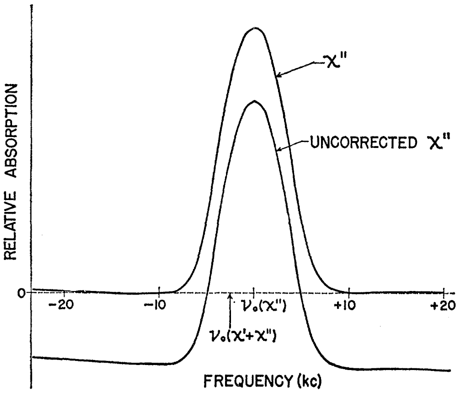


FIG. 2. Resolved nuclear resonance absorption spectrum, $\chi''(\nu)$, in an aluminum single crystal for the magnetic field along the [001] direction (upper curve) and the same spectrum uncorrected for the finite frequency range of the experimental data (lower curve). $\nu_0(\chi'')$ is the resonant frequency of $\chi''(\nu)$ [the frequency at which $d\chi''(\nu)/d\nu=0$]. $\nu_0(\chi'+\chi'')$ is the corresponding "resonant frequency" of the spectrometer recording in Fig. 1. $[\nu_0(\chi'+\chi'')-\nu_0(\chi'')]$ is the eddy current shift, $\Delta\nu_{ec}$.

from positive values. We denote this curve by $f(\nu)_{\text{exp}}$. If one draws in the baseline indicated by the experimental data, then substitution of $f(\nu)_{\text{exp}}$ in Eqs. (1) and (2) leads to the $\chi''(\nu)$ shown by the lower curve in Fig. 2. This curve is qualitatively of the expected form, but the baseline is slightly tilted in the clockwise direction and lies below the zero absorption line. This may be explained as follows. In Fig. 1, using the experimental baseline we find that the area under the positive part of $f(\nu)_{\text{exp}}$ is less than the area under the negative part by about 20%. This indicates that the true baseline lies slightly below the experimental baseline and that the noise is obliterating the portions of the high- and low-frequency tails that lie beyond the experimental frequency range shown in Fig. 1. We assume that the true baseline lies below the experimental baseline by an unknown amount k, where k is a positive constant. Then the true $f(\nu)$ is equal to $f(\nu)_{\text{exp}}+k+$tails. By substituting $f(\nu)_{\text{exp}}$ in Eqs. (1) and (2), one is neglecting k and the tails. In Eq. (1), the effect of neglecting k is to cause the resultant χ'' to be slightly tilted in the clockwise direction, and the effect of neglecting the tails is to cause the resultant χ'' to be moved algebraically downward with no change in shape. In Eq. (2), the combined effect of neglecting k and the tails is to cause the resultant χ'' to be moved algebraically downward with only negligible change in shape. [This can be demonstrated analytically for reasonable forms for the tails of $f(\nu)$ such as ν^{-2} or ν^{-3}.] To correct for these effects, we first pick that value of k that untilts the χ'' curve. Typical values of k that result are 1% or less of the peak height of the original experimental curve, or of the order of the noise. Then, on the assumption that χ'' has reached zero absorption when it has become essentially constant with frequency (an assumption implicit in work on thin samples as well), we move the untilted χ'' upward until the constant regions of χ'' are at zero absorption. The final corrected χ'' is the upper curve in Fig. 2. It may be noticed that since χ'' is zero beyond about ±10 kc/sec from $\nu_0(\chi'')$, the highest and lowest 30% or so of the frequency range in Fig. 1 corresponds to pure $d\chi'/d\nu$. The "resonant frequency," $\nu_0(\chi'+\chi'')$, of the experimental derivative curve in Fig. 1 is indicated in Fig. 2 to demonstrate the frequency shift due to eddy currents.[3,4]

RESULTS FOR ALUMINUM AND COPPER

Measurements were made on aluminum and copper single crystals at room temperature and a fixed magnetic field of 12.0 kG with a conventional Pound spectrometer using a modulation frequency of 280 cps, modulation amplitude 2.0 G peak-to-peak, and output time constant 66 sec. The total frequency range of the data is

TABLE I. The Knight shifts, linewidths, and second moments of the nuclear magnetic absorption spectra, $\chi''(\nu)$, in aluminum and copper single crystals for the magnetic field parallel to the [001], [$\bar{1}$11], and [$\bar{1}$10] directions, compared with the powder results.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
							Second moment of $\chi''(\nu)$	
Nucleus	Direction parallel to mag. field	Knight shift of $\chi''(\nu)$[a] $\Delta H/H$ (%)	Eddy current shift $\Delta\nu_{ec}$ (kc/sec)	Linewidth of $\chi''(\nu)$ $\delta\nu$ (kc/sec)	$\dfrac{\Delta\nu_{ec}}{\frac{1}{2}\delta\nu}$	$\dfrac{\frac{1}{2}\delta\nu}{[\langle(\Delta\nu)^2\rangle_{\text{th}}]^{\frac{1}{2}}}$	Theor. dipolar $\langle(\Delta\nu)^2\rangle_{\text{th}}$ (kc/sec)^2	Experimental[b] $\langle(\Delta\nu)^2\rangle_{\text{exp}}$ (kc/sec)^2
Al^{27}	[001]	0.168±0.002	−2.54±0.10	8.0±0.1	0.64±0.03	1.54±0.02	6.76	8.3±0.7
	[$\bar{1}$11]	0.168±0.003	−3.34±0.15	9.8±0.1	0.68±0.03	1.50±0.02	10.6	12.3±1.2
	[$\bar{1}$10]	0.168±0.003	−3.70±0.15	9.9±0.1	0.75±0.03	1.59±0.02	9.67	12.2±1.5
	Powder	0.164±0.001	...	9.5±0.1	...	1.57±0.02	9.15	11.8 [c]
Cu^{63}	[001]	0.232±0.003	−1.67±0.10	5.6±0.1	0.60±0.04	1.23±0.02	5.21	6.3±0.6
	[$\bar{1}$11]	0.234±0.003	−2.47±0.15	7.7±0.1	0.64±0.04	1.35±0.02	8.19	8.5±1.0[d]
	[$\bar{1}$10]	0.234±0.002	−2.33±0.15	7.4±0.1	0.63±0.04	1.36±0.02	7.45	8.0±1.0[d]
	Powder	0.234±0.001	...	7.1±0.1	...	1.34±0.02	7.04	8.2±0.4

[a] Relative to 1N solution of $AlCl_3$ in 0.01N $FeCl_3$, and CuCl powder, respectively.
[b] Corrected for modulation peak-to-peak amplitude of 2.0 G.
[c] Average of two values reported in the literature.
[d] Second moment from one run only.

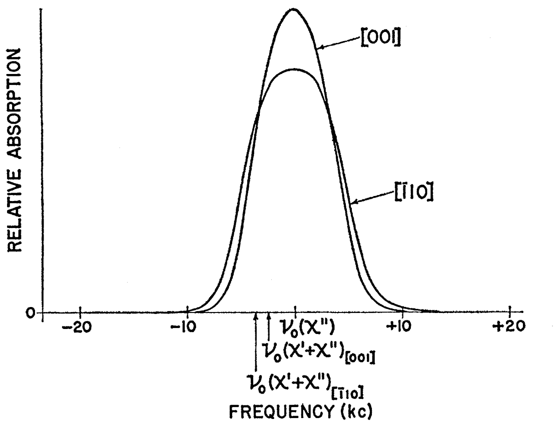


FIG. 3. Resolved nuclear resonance absorption spectra, $\chi''(\nu)$, in an aluminum single crystal for the magnetic field parallel to the [001] and [1̄10] directions. The areas under the two curves are equal. $\nu_0(\chi'')$ is the resonant frequency of $\chi''(\nu)$ [the frequency at which $d\chi''(\nu)/d\nu=0$]. $\nu_0(\chi'+\chi'')_{[001]}$ and $\nu_0(\chi'+\chi'')_{[\bar{1}10]}$ are the "resonant frequencies" of the experimental derivative curves for the [001] and [1̄10] directions, respectively. $[\nu_0(\chi'+\chi'')-\nu_0(\chi'')]$ is the eddy current shift, $\Delta\nu_{ec}$.

about 45 kc/sec for aluminum and 30 kc/sec for copper. The single crystals are $\frac{1}{2}$ in. diam and $\frac{3}{4}$ in. long, with the [110] direction parallel to the axis of symmetry. They are inserted in the probe coaxially with the rf coil so that the rf magnetic field is parallel to the cylindrical surface of the crystals. The resulting signal-to-noise ratio is about 100 to 150 in aluminum and 50 to 75 in copper, depending on orientation.

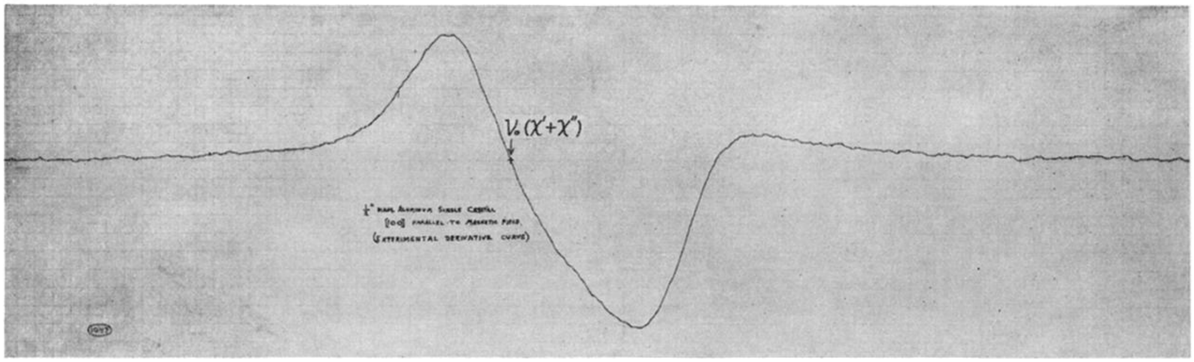
We have determined the absorption spectra, $\chi''(\nu)$, for the fixed magnetic field parallel to the [001], [1̄11], and [1̄10] directions. Examples of such $\chi''(\nu)$ curves are shown in Fig. 3. All the $\chi''(\nu)$ curves for both aluminum and copper are very symmetrical except in the regions of the tails where the experimental uncertainty is relatively large. The line shapes in aluminum and copper powders are also symmetrical, as is well known, but the line shape in aluminum powder is considerably more rectangular than in copper powder. In the copper single crystal, we find that the [1̄11] and [1̄10] line shapes are almost identical and are only slightly flatter at the top than the [001] shape. The shapes in all three directions are very similar to the shape in copper powder. In the aluminum single crystal, however, the [001] shape is very similar to the copper shapes, whereas the [1̄11] shape is somewhat more rectangular and the [1̄10] shape is considerably more rectangular. The latter may be seen in Fig. 3. These results indicate that the mechanism that causes the pronounced difference in line shape between aluminum and copper powders is not isotropic.

Table I lists the results for the Knight shifts, linewidths, second moments, and eddy current shifts in aluminum and copper for the [001], [1̄11], and [1̄10] directions, together with the powder results for comparison. The tabulated data are the averages of two runs for aluminum and three runs for copper, except where noted otherwise. Column 3 shows that the Knight shifts for both aluminum and copper are isotropic and equal to the powder values, within the small experimental uncertainty. While an anisotropic Knight shift in aluminum and copper is not impossible in principle, it is unlikely, and the close agreement of the Knight shifts for the three orientations and powder, despite a considerable variation in the magnitude of the eddy current shift with crystal orientation, is unlikely to be an accident and is the best test we have of the validity of the method of resolving $\chi''(\nu)$. Column 4 gives the eddy current shifts, $\Delta\nu_{ec}=\nu_0(\chi'+\chi'')-\nu_0(\chi'')$ (see Fig. 3), which are seen to vary with orientation. The linewidths, $\delta\nu$, (peak-to-peak separation in $d\chi''/d\nu$), are given in column 5. $\Delta\nu_{ec}$ would be proportional to $\delta\nu$ for constant line shape. From column 6, this is seen to be true for copper but not for aluminum where the line shape changes appreciably with orientation, as mentioned above. Column 7 shows that the linewidths vary with direction approximately but not exactly as the square root of the theoretical dipolar second moments, which are given in column 8. Column 9 gives the experimental second moments. Within their large uncertainty, they vary in proportion to the theoretical dipolar second moments, but in most orientations are definitely larger, which is well known to be the case in the powders. The uncertainties in the experimental second moments are too large to permit a significant determination of the orientation dependence of the excess broadening.

CONCLUDING REMARKS

The thick-sample method appears to be applicable to a number of pure metals and alloys, in single crystal or polycrystalline form. In cases where the signal-to-noise ratio is unfavorable, the simple geometry used in the aluminum and copper experiments would not be adequate. However, the total surface of the sample can be increased by cutting slots in the crystal or by stacking a number of thick crystals. Anisotropic effects in single crystals of noncubic metals will be of particular interest. Pure quadrupole resonance and relaxation time measurements on metallic single crystals should also be possible.

We are indebted to Dr. Ralph J. Harrison for valuable discussions, to Mrs. Anna Hansen for carrying out the numerical computations, to John DeMarco for orienting the single crystals, and to Kenneth L. Blacker for his help in the experimental program.



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