NUCLEAR MAGNETIC RESONANCE IN BISMUTH METAL AT 4.2°K†

R. R. Hewitt and B. F. Williams
Department of Physics, University of California, Riverside, California
(Received 30 January 1964)

We report the measurement of the nuclear magnetic resonance (nmr) spectrum of pure bismuth metal powder at 4.2°K. The existence of a large quadrupole interaction in bismuth has been expected since the nmr measurements[1] of liquid bismuth showed a loss of the signal when the metal solidified. The specific-heat measurements of bismuth have also shown a large T^{-2} term associated with the nuclear quadrupole interaction.[2,3] The nmr measurements in indium metal powder[4] indicate the feasibility of nmr with large quadrupole interactions.

The bismuth sample used was prepared from zone-refined metal; the 40-micron powder was annealed in a carbon boat under vacuum at 210°C for six hours. The nmr measurements were made with a conventional Pound-Knight marginal oscillator and phase-sensitive detector. A partial spectrum of the bismuth measurements at the resonant frequency ν_R of 16 Mc/sec is shown in Fig. 1.

Analysis of the nmr spectrum is quite similar to the method outlined by Jones, Graham, and Barnes.[5] Through third-order perturbation theory,[6] the splitting of the $(\frac{1}{2}$-$\frac{1}{2})$ transition $\Delta\nu_{HL}$ is given by

$$\Delta\nu_{HL}/\nu_R = 25b/9\nu_R^{\,2} - \tfrac{5}{3}a, \qquad (1)$$

where

$$b = \tfrac{1}{16}\nu_Q^{\,2}[I(I+1) - \tfrac{3}{4}], \quad a = K_{\rm ax}/(1+K_{\rm iso}),$$

$$\text{and } \nu_Q = 3e^2qQ/2I(2I-1)h.$$

Figure 2 shows a plot $(\Delta\nu_{HL})(\nu_R^{-1})$ vs ν_R^{-2}. The intercept at the origin of ν_R^{-2} gives the measure of a, essentially the axially symmetric anisotropic Knight shift $K_{\rm ax}$, and the slope of the straight line gives b, the measure of ν_Q. The values from this plot are $K_{\rm ax} = -2.7\,\%$ and $\nu_Q = 2.40$ Mc/sec. The isotropic Knight shift $K_{\rm iso}$ may be obtained from the $(\frac{1}{2}$ - $\frac{1}{2})$ extremum positions ν_H and ν_L by the following relations[5]:

$$K_H = (\nu_H - \nu_R)/\nu_R = K_{\rm iso} - a + b/\nu_R^{\,2} \qquad (2)$$

and

$$K_L = \frac{\nu_R - \nu_L}{\nu_R} = -K_{\rm iso} - \tfrac{2}{3}a + \frac{16b}{9\nu_R^{\,2}} - \frac{a^2\nu_R^{\,2}}{4b}. \qquad (3)$$

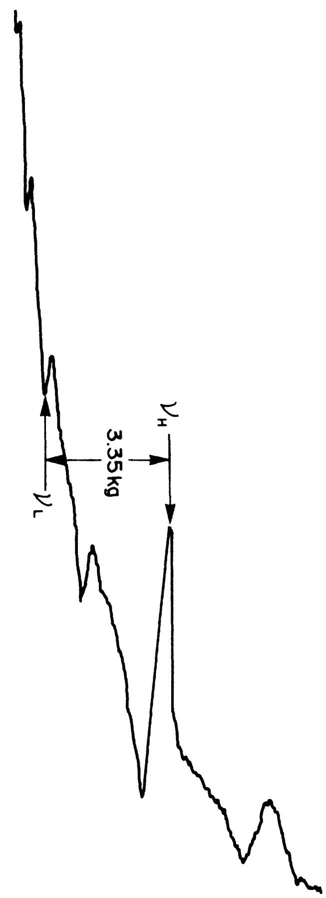

FIG. 1. A recorder trace of the derivative of a partial spectrum of the nmr of ^{209}Bi at 4.2°K at a resonant frequency of 16 Mc/sec. The modulation here was 40 gauss peak to peak. The range of field in this trace is 27 to 17 kG; the nonlinearity of the sweep is due to the magnet saturation. The rapidly drifting baseline is due to the field dependence of the rf magnetoresistance of bismuth.

A fit of ν_L and ν_R to (2) and (3) using the values of b and a determined from (1) gives $K_{\rm iso} = -0.3 \pm 0.2\,\%$. As indicated by the average error, the scatter in this result is large as can be expected from the width of the lines measured. The reference used was ^{209}Bi in an aqueous solution of $Bi(NO_3)_3$ at room temperature.

Finally it is possible to obtain an independent measurement of the quadrupole coupling from the nmr spectrum. The position of the satellite

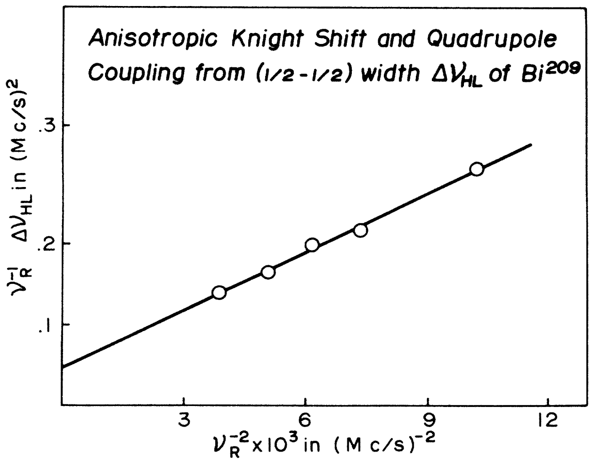

FIG. 2. Plot of the separation of the $(\frac{1}{2}-\frac{1}{2})$ transition of ^{209}Bi at 4.2°K. The range of resonant frequencies is 9.85 Mc/sec to 16.00 Mc/sec.

maxima of the powder pattern occuring when the principal axis of the field gradient tensor and the magnetic field are perpendicular, through the third order of perturbation theory, is given by

$$\nu(m \leftrightarrow m-1)$$

$$=\nu_R\{1-[a+\tfrac{1}{2}(\nu_Q/\nu_R)(m-\tfrac{1}{2})]$$

$$-\tfrac{1}{16}(\nu_Q/\nu_R)^2[3m(m-1)-I(I+1)+\tfrac{3}{2}]\}, \qquad (4)$$

and the separation of pairs of corresponding satellites is given by $\frac{1}{2}\nu_Q(2m-1)$. The value of ν_Q was determined from different pairs of satellites over the same frequency range with the result $\nu_Q = 2.44 \pm 0.07$ Mc/sec in agreement with the value from the $(\frac{1}{2}-\frac{1}{2})$ width.

The value of the quadrupole coupling e^2qQ/h of 58.5 ± 2 Mc/sec is higher by about a factor of two than the values estimated from the T^{-2} term of the specific heat. A correction for this term in the bismuth specific-heat data will make an appreciable change in the electronic specific-heat values. This quadrupole coupling will also be useful in checking any model of the electronic structure as has been done for antimony.[7]

The anistropic Knight shift is an order of magnitude larger than any that have been reported to date. The isotropic Knight shift is the only reported shift that is appreciably different in the solid from that in the liquid state. In order to check these anomalies and because of the need for a temperature dependence study of these shifts, we are initiating a measurement of nmr in a single crystal of bismuth.

---

†Work supported in part by the National Science Foundation. The electromagnet used in this research was purchased through an equipment grant of the Advanced Research Projects Agency.

[1]W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) 8, 173 (1959).

[2]N. Phillips, Phys. Rev. 118, 644 (1960).

[3]D. Weiner, Phys. Rev. 125, 1226 (1961).

[4]D. R. Torgeson and R. G. Barnes, Phys. Rev. Letters 9, 255 (1962).

[5]W. H. Jones, Jr., T. P. Graham, and R. G. Barnes, Phys. Rev. 132, 1898 (1963).

[6]M. H. Cohen and F. Reif, Solid State Physics (Academic Press Inc., New York, 1957), Vol. V.

[7]E. H. Hygh and T. P. Das (to be published).

TRANSMITTED PHONON DRAG EFFECT IN GERMANIUM AT VERY LOW TEMPERATURES

Edward J. Walker and Robert W. Keyes
IBM Watson Research Center, Yorktown Heights, New York
(Received 3 February 1964)

Extensive measurements of the phonon drag contribution to the thermoelectric power in relatively pure germanium have been carried out by Geballe and Hull.[1] It is rather difficult to extend such measurements to degenerately doped germanium because the normal electronic thermoelectric pwer obscures the phonon drag effect in heavily doped material. We have been able to extend phonon drag measurements to degenerate germanium at very low temperatures by using the transmitted phonon drag effect originated by Hubner and Shockley.[2] In the transmitted phonon drag effect the phonon part of the Peltier coefficient can be measured independently of any electronic contribution.

We prepared germanium n-p-n structures by depositing layers of heavily doped n-type germanium on both sides of p-type wafers by the iodide vapor growth method.[3] The carrier concentration in the n-type layers was 6.5×10^{18} cm^{-3} and