at an appreciable rate.

We wish to acknowledge the assistance of L. Kopf in the preparation of the tunnel units, and discussions with V. Ambegaokar. B. D. Josephson informs us that he has independently reached some of the theoretical conclusions of the last few paragraphs.

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## NUCLEAR MOMENT OF $Ni^{61}$ FROM NUCLEAR RESONANCE STUDIES IN STEADY EXTERNAL MAGNETIC FIELDS

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Recently the determination of the nuclear moment of $Ni^{61}$ has become of particular interest. Orton, Auzins, and Wertz[1] from an electron spin resonance study of the hyperfine splitting of $Ni^{+2}$ in MgO and a comparison of the hyperfine splitting of $Ni^{+2}$ with $Co^{+1}$ estimated a nuclear moment of $Ni^{61}$ of 0.3 nm. Bennett and Streever[2] re-examined the electron spin resonance spectra of nickel in MgO and nickel in germanium, and proposed that the previously estimated value of 0.3 nm for the nuclear moment of $Ni^{61}$ was in error by a factor of three, and that a value 0.9 nm was more consistent with the published spectra. Of course, associated with both values, the 0.3 nm and 0.9 nm, one expects possibly an error of about 20% associated with a comparison of isoelectronic atoms. A knowledge of the nuclear moment of $Ni^{61}$ is important for an understanding of hyperfine fields in ferromagnetic metals and alloys. In order to clear up this ambiguity in the nuclear moment, we have studied the nuclear magnetic resonance of $Ni^{61}$, using free precession equipment, in applied external magnetic fields of up to 10 000 gauss. At 77°K we find above about 2500 gauss that the resonance frequency $\nu$ varies linearly with applied external field at a rate of $0.354 \pm 0.020$ Mc/kG-sec, corresponding to an uncorrected nuclear moment of $0.70 \pm 0.04$ nm. Corrections on this value are discussed below.

The $Ni^{61}$ nuclear resonance was observed using standard free precession equipment consisting of a pulsed rf oscillator operating at about 300 volts rf and suitable receiving equipment. Separate sending and receiving coils were used, the coil geometry being such that the coils were coaxial along an axis at right angles to the direction of the externally applied dc field $H_0$.

The sample consisted of about 2 grams of nickel powder with a particle diameter of about 10 $\mu$ which was isotopically enriched to about 100% in the isotope 61. The free precession echo signal was observed directly on the oscilloscope and heterodyned with a known frequency. In Fig. 1 we plot resonance frequency against externally applied dc magnetic field at 77°K, where the frequency was measured up to 10 000 gauss. Above approximately 2500 gauss, the resonance frequency $\nu$ varies linearly with applied field at a rate of $0.354 \pm 0.02$ Mc/G-sec. The indi-

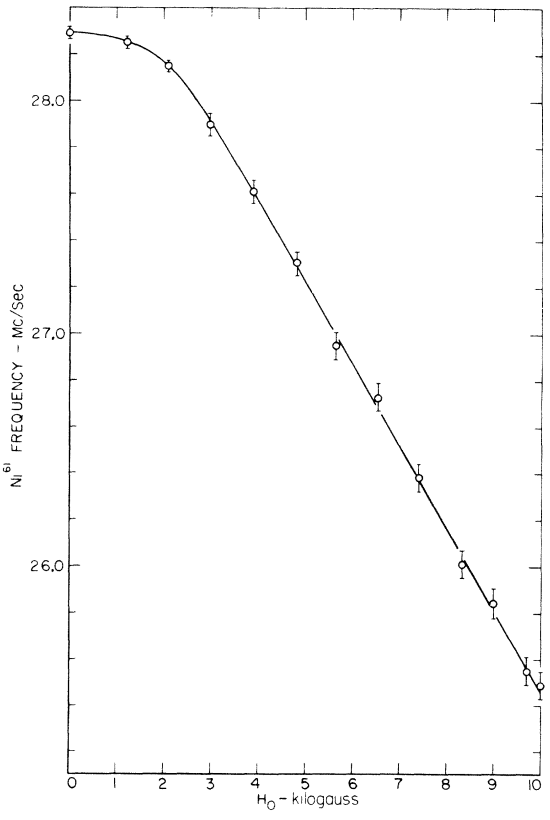


FIG. 1. Resonance frequency $\nu$ plotted against external dc field $H_0$ at 77°K.

cated uncertainties in the slope are limits of error obtained directly from the estimated maximum imprecision in the measured frequencies. The linewidth at zero applied field calculated from the width of the echo is about 140 kc/sec, if one assumes a Lorentz line shape. As the applied field is increased, the linewidth increases to a value of about 300 kc/sec at 2500 gauss, at which point it remains essentially constant up to the highest dc field applied. The signal intensity decreases with increased external field. The signal intensity at 10 000 gauss is sufficiently low that accurate frequency measurements become more difficult. Similar results were observed at room temperature, where the slope of the linear portion of the frequency vs field curve was found to be the same within the experimental error. However, due to a smaller signal intensity, measurements were made only with external fields less than 7000 gauss.

The interpretation is as follows: At high power levels and in zero applied field the resonance is mostly from nuclei in domains and partly from nuclei in domain walls. In a multidomain particle, nuclei in domains and in domain walls are expected to have very nearly the same frequency in zero applied field. The shift of the resonance to lower frequencies as the external field is applied has already been observed by Budnick[3] and attributed to a negative hyperfine field at $Ni^{61}$ (that is, the nuclei are aligned oppositely to the electronic magnetization). Budnick, however, due to a smaller nuclear signal (associated with the use of continuous wave equipment), was not able to follow the resonance up to as high a dc field and establish a value for the nuclear moment. When the external field is applied, the domains become aligned preferentially along the applied field direction, and since the hyperfine field is negative, the applied field decreases the resonance frequency for nuclei in domains. The effect of the external field will, however, be initially compensated by demagnetization fields and by the fact that the domains are oriented in all possible directions with respect to the applied field. In fields above about 2500 gauss, the particles are essentially uniformly magnetized, and the resonance frequency will be given by

$$\omega = \gamma[H_n - (H_0 - H_d)]. \quad (1)$$

Here $H_n$ is the nuclear hyperfine field, and the demagnetizing field $H_d$ has a maximum value $\frac{4}{3}\pi M$ for spherical particles. From the slope of the linear portion of the curve of Fig. 1, we calculate a moment $0.70 \pm 0.04$ nm.

Assuming that the particles are spherical, we can use the experimental data to calculate a value of $\frac{4}{3}\pi M$ for nickel. The value of $\nu$ at $H_0 = 0$ obtained from the intercept of Fig. 1 is 28.99 Mc/sec, while in the domain walls the resonance frequency is about 28.28 Mc/sec at 77°K. From the difference of 0.71 Mc/sec, we obtain a value of 2.01 kG for $\frac{4}{3}\pi M$ which agrees to within six percent with values given in the literature[4] for $\frac{4}{3}\pi M$ at 77°K.

Equation (1) is not exactly valid if we consider the effect of $(H_0 - H_d)$ on the hyperfine field. The effect of the net external field may give rise to a contribution to the hyperfine field proportional to the net applied field. This field would arise through polarization of the conduction electrons by the applied field which would give rise to a field at the nucleus proportional to the net applied field (the ordinary Knight shift). This effect, which is probably not more than a percent or so of the applied field, results in a corresponding correction to the nuclear moment. A positive Knight shift of this sort would result in an actual moment smaller than that reported. A negative Knight shift, which might be expected to be larger than the positive shift, would result in a moment larger than that reported.

Large rf pulse amplitudes are necessary, because nuclei in the bulk of the sample experience not the large enhancement of the rf level found for nuclei in the domain walls, but a smaller enhancement resulting from rotations of the electronic magnetization in the applied and the anisotropy field. Robert[5] finds for these nuclei an enhancement $\eta$ of the applied rf field $H_1$ given by

$$\eta = H_n/(H_0 + H_A), \quad (2)$$

where $H_n$ is the nuclear hyperfine field and $H_A$ is the anisotropy field. At the lower applied fields, the maximum pulse amplitudes used were sufficiently large to fulfill the requirements necessary to observe the maximum spin echo. As the rf enhancement decreased in accordance with Eq. (2), the rf levels fell short of this with a consequent reduction in signal intensity.

The nuclear moment 0.70 nm that we obtain lies within about 20% of the value suggested in reference 2 and strongly supports the arguments of that paper.

Using a value for the nuclear moment of 0.70 nm, the hyperfine fields at the $Ni^{61}$ nuclei in pure nickel and for small concentrations of nickel in

Table I. Resonance frequencies and hyperfine fields at $Ni^{61}$ nucleus at 77°K in pure nickel and for small concentrations of $Ni^{61}$ in cobalt and iron using a moment 0.70 nm.

| | $\nu$ (Mc/sec) | $H_n$ (kilogauss) |
|---|---|---|
| $Ni^{61}$ in nickel | 28.3 | 80 |
| $Ni^{61}$ in cobalt | 71.7 | 203 |
| $Ni^{61}$ in iron | 89.1 | 252 |

cobalt[6] and iron[7] can be recalculated and are given in Table I, along with the resonance frequency, both at 77°K, which to within one percent is equal to the value at 0°K.

The hyperfine fields in Table I are seen to be readily understandable compared to those at $Co^{59}$ and $Fe^{57}$ nuclei in pure iron and pure cobalt and in the dilute alloys, if one uses the general idea that hyperfine fields are proportional to local moments. This idea has already been discussed in reference 7, where hyperfine fields (based on a moment 0.9 nm for nickel) are compared. The results are somewhat changed with the moment 0.70 nm, and this will be discussed at a later time. Also, the spin-echo method of observation permits the direct measurement of $T_1$ and $T_2$. Measurements of $T_1$ and $T_2$, together with the discussion of linewidths as a function of field, will also be discussed in greater detail at a later time.

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## THERMAL EXPANSION OF GERMANIUM*

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In many isotropic materials the thermal expansion coefficient is negative at low temperatures, e.g., vitreous silica[1] below 200°K, indium antimonide[1] below 55°K, silicon[1] below 120°K, germanium[1,2] below 40°K, and ice[3] below 60°K. These examples of an over-all lattice contraction are distinct from the metals plutonium, chromium, and Invar, where negative coefficients arise from magnetic interactions or from the electron gas, and are also distinct from highly anisotropic crystals such as cadmium or zinc in which the coefficient may be negative in one direction even though the volume coefficient, $\beta$, remains positive.

We define the average Grüneisen parameter by

$$\gamma = \beta V/\kappa_T C_V,$$

where $C_V$ is the specific heat of volume $V$ and $\kappa_T$ is the isothermal compressibility. If $C_i$ is the contribution of the $i$th mode to the specific heat, we may also write

$$\gamma = \sum \gamma_i C_i / \sum C_i,$$

where

$$\gamma_i = -d \ln \nu_i / d \ln V$$

is the logarithmic rate of change of lattice frequency with volume. Blackman[4] and Barron[5] have each discussed theoretical models for which $\gamma_i$ is negative for certain transverse vibrational modes. If the relative contribution of such modes to the specific heat is sufficiently important at low temperatures, then the average $\gamma$ or observed expansion coefficient may be negative.

Sheard[6] has shown how individual $\gamma_i$ and the limiting averages at high and low temperatures, $\gamma_\infty$ and $\gamma_0$, can be calculated from the pressure derivatives of the elastic constants. This procedure has given substantially correct results for