Temperature Dependence of Co^{59} Nuclear Magnetic Resonance in Single-Domain Cobalt Particles*

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The temperature dependence of the nuclear magnetic resonance (NMR) frequency of Co^{59} nuclei in single-domain particles of fcc cobalt metal has been measured in the temperature range between 4.2 and 570°K, using a conventional super-regenerative oscillator spectrometer. Two surprising results have emerged. First, the normalized fractional decrease of the resonance frequency, $\Delta(T)=[\nu(T)-\nu(0)]/\nu(0)$, can be quite accurately fitted by the simple expression $\alpha T^{3/2}$ to temperatures as high as about 450°K, with $\alpha=(4.87\pm0.01)\times10^{-6}(°K)^{-3/2}$. Second, when these measurements are compared with earlier studies of the temperature dependence in walls of multidomain-Co particles, it is found that the $\Delta(T)$ in single-domain particles is greater than that in walls at all temperatures.

I. INTRODUCTION

SINCE the first successful NMR observation of Co^{59} nuclei in fcc cobalt metal, NMR in magnetic materials has become one of the most powerful probes for investigating the static and dynamic characteristics of ordered magnetic materials.[1] The temperature dependence of the NMR frequency should provide a most accurate measure of the temperature dependence of the saturation magnetization. Indeed, a large number of experiments have been done in the ferromagnetic metals Fe, Co, and Ni. These studies were, however, limited to multidomain samples, until Gossard *et al.* succeeded in observing the resonance from Co^{59} nuclei in single-domain cobalt particles.[2]

We present here the first extensive measurements of the temperature dependence of the NMR frequency in single-domain particles of a ferromagnetic metal. The four samples studied consisted of dispersed fcc cobalt particles with average diameters, as determined by electron microscopy, ranging from 120 to 222 Å. Their resonances were studied in the temperature range between 4.2 and 570°K. The samples and the experimental technique are described in Sec. II. The NMR spectrum of each sample and the temperature dependence of its resonance frequency, including comparison with NMR in domain walls of multidomain particles, are given in Sec. III.

II. EXPERIMENTAL PROCEDURE

A. Samples

The samples examined in the present work were prepared in a manner similar to that described by Gossard *et al.*[2] In order to determine the size distributions for the fine particles, both electron microscopy and x-ray diffraction studies were carried out on the four samples used. The electron microscope specimens were prepared by plotting the sample in a resin (Douglass and Sturgess Clear Casting Resin No. 23) and slicing off thin (600–900 Å) sections with an LKB Ultrotome III using a diamond knife. Micrographs of the specimens were taken with a Japan Electron Microscope 6A electron microscope. These showed that the particles were not uniformly distributed but tended to occur near the edge of large masses of the γ-alumina support material. Because the cobalt particles, particularly the smaller ones, were difficult to distinguish from the γ-alumina, only those areas of the micrographs which showed particles relatively free from the support were used for sizing. Particle-size histograms for the four samples are shown in Fig. 1. Average particle diameters were also determined from the broadening of the (111) cubic cobalt x-ray diffraction line. The average particle sizes obtained from the x-ray analysis and volume-weighted averages, $\langle d\rangle_v=\sum_i N_i d_i^4/\sum_i N_i d_i^3$, calculated from the electron microscope histograms, are given in Table I. The discrepancy between the x-ray and electron microscope sizes seen in Table I could be caused by the particles not being single crystals or containing some other contribution to the x-ray linewidth, such as stacking faults. Electron diffraction patterns of the samples indicate the presence of Co_3O_4 in addition to fcc cobalt metal.

TABLE I. Average particle diameters of studied samples.

Sample No.	x-ray size (Å)	Electron microscope size (Å)
A	140	222
B	70	145
C	50	140
D	50	120

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[1] A. M. Portis and R. H. Lindquist, in *Magnetism, A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 2A, p. 375.
[2] A. C. Gossard, A. M. Portis, M. Rubinstein, and R. H. Lindquist, Phys. Rev. 138, A1415 (1965).

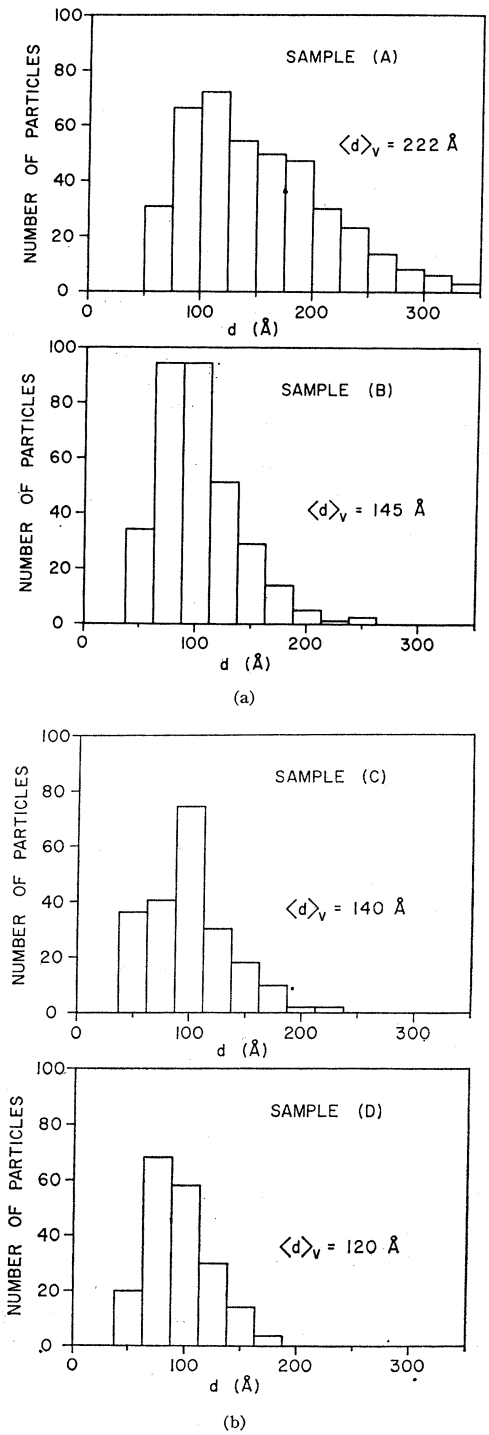

FIG. 1. Particle-size distributions from electron micrographs. $\langle d \rangle_v = \Sigma_i N_i d_i^4 / \Sigma_i N_i d_i^3$.

B. Experimental Technique

The Co^{59} NMR signal was observed by using a conventional frequency-modulated push-pull super-regenerative oscillator followed by a synchronous detection system. The circuit diagram of the oscillator spectrometer used in this study is shown in Fig. 2. The frequency was modulated at 40 Hz with a maximum modulation amplitude of about 10 MHz in the region of 200-MHz oscillation, and quenched at 40–700 kHz by sine wave. For the study of the temperature dependence of the signal, a rejective audio amplifier, which rejects both first and second harmonics of the modulation frequency, was used. By using a 10-MHz modulation amplitude, the entire signal of sample C, for example, could be displayed on the oscilloscope with a signal-to-noise ratio of about 5 at room temperature. The signal-to-noise ratio was further improved by a factor of 10 with a "wave-form eductor" (Princeton Applied Research, Model TDH 9). The rejection of first and second harmonics discriminates against the relatively smooth frequency-dependent loss because of the ferromagnetic material present. This would otherwise result in a large background when the modulation amplitude is greater than the linewidth, as it is in this case. The temperature dependence of the NMR frequency was studied using the signal on the oscilloscope with changing temperature of the sample. Temperatures were obtained with liquid He, liquid H_2, and, in the case of higher temperatures, with a commercial temperature controller (Varian Model V-4540) which was calibrated with chromel-alumel thermocouples.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Resonance Spectrum and External Field Dependence

It is very difficult to obtain a true line shape using a super-regenerative spectrometer, unless the line is so narrow that each sideband can be completely resolved, However, if the quench frequency is very small compared to the linewidth, a rough resonance spectrum can be obtained using conventional phase-sensitive detection of the first harmonic. In order to get a rough resonance spectrum of the four samples, the first derivative of the absorption signal was obtained using a 50-kHz quenching frequency and 500-kHz modulation amplitude. These are both fairly small compared to the linewidth. The points shown in Fig. 3 were determined by substracting the base line, obtained under the same conditions but without sample, every 500 kHz. These spectra were obtained at a temperature of 77°K. It is clear from Fig. 3 that the spectrum of sample A is quite asymmetrical, showing a long tail and bump on the low-frequency side. The histogram for this sample also indicates a greater fraction of larger particles which might give rise to such an asymmetry. The bump and long tail on the low-frequency side may be due to resonance from particles larger than single domain.

In order to make sure that the resonances of samples B, C, and D were associated with NMR from single-domain particles, the external field dependence of the

resonance frequency was studied up to 8 kOe. The results agree with those of previous studies.[2]

B. Temperature Dependence of Resonance Frequency

The temperature dependence of the Co^{59} NMR frequency at zero external field has been studied in greatest detail for sample C. In the present experiment, it is very difficult to determine the *exact* center of the resonance, since the linewidth is too wide ($\Delta\nu \approx 2$ MHz) and the signal is complicated by the super-regenerative detection and the rejection of the fundamental- and second-harmonic components of the absorption signal. However, since the shape of the oscilloscope display was not observed to change substantially with temperature, the point where the signal passed through zero on the oscilloscope was chosen. The frequency of this point was measured at each temperature by obtaining zero beat with a standard signal generator. The frequency of the main signal could be easily distinguished from the sideband signals by varying the quench frequency. When this is done, the main signal

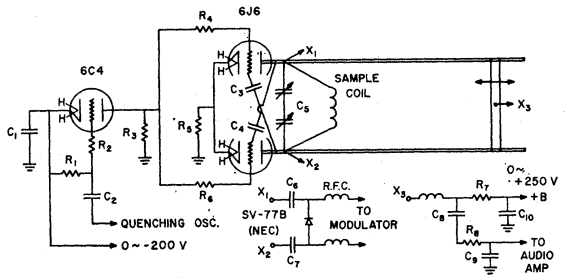

FIG. 2. Circuit diagram of the spectrometer ($R_1=100$ kΩ, $R_2=100\,\Omega$, $R_3=R_4=R_6=10$ kΩ, $R_5=100\,\Omega$, $R_7=5$ kΩ, $R_8=100$ kΩ, $C_1=0.1$ μF, $C_2=1000$ pF, $C_3=C_4=10$ pF, $C_5=5$–20 pF variable, $C_6=C_7=10$ pF, $C_8=0.1$ μF, $C_9=0.001$ μF, $c_{10}=1000$ pF).

remains stationary while the sidebands move. We are mainly interested in the fractional decrease of the resonance frequency with temperature, $\Delta(T)=[\nu(T)-\nu(0)]/\nu(0)$, and believe that the relative error in $\Delta(T)$ is less than 1% at all temperatures. Measurements were also made on samples B and D at several temperatures. It was found that their $\Delta(T)$'s were the same as for sample C within our stated error of 1%. The resonance frequency extrapolated to 0°K is estimated to be 222.2±0.5 MHz for all samples. This corresponds to a hyperfine field of −221.0±0.5 kOe. Our observed $\Delta(T)$ for single-domain particle sample C, together with earlier studies on multidomain particles,[3] are shown in Fig. 4. It was impossible to measure accurately the temperature dependence of sample A, because its NMR spectrum was very broad and complicated by the presence of multidomain particles.

[3] V. Jaccarino, Bull. Am. Phys. Soc. 4, 461 (1959).

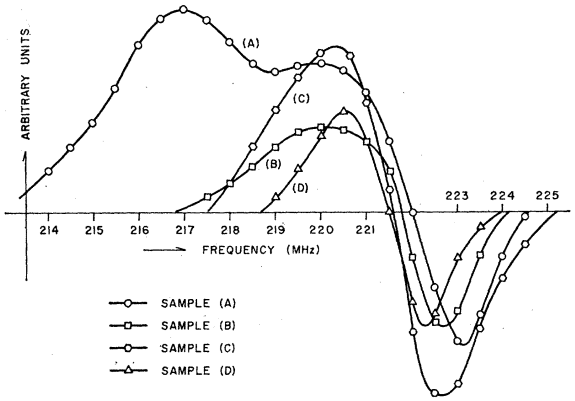

FIG. 3. Co^{59}-NMR spectra of the single-domain cobalt particle samples at 77°K.

The normalized fractional decrease of resonance frequency with temperature is seen to fit quite accurately a simple $T^{3/2}$ relation with the coefficient $\alpha=(4.87\pm0.01)\times10^{-6}(°K)^{-3/2}$ to temperature as high as 450°K. Samples B–D do not differ greatly in average particle size; however, they all showed the same temperature coefficient within the accuracy of our measurements. It thus appears that there is no sensible size dependence of this coefficient.

Figure 4 also shows that the NMR frequency in single-domain particles decreases more rapidly with

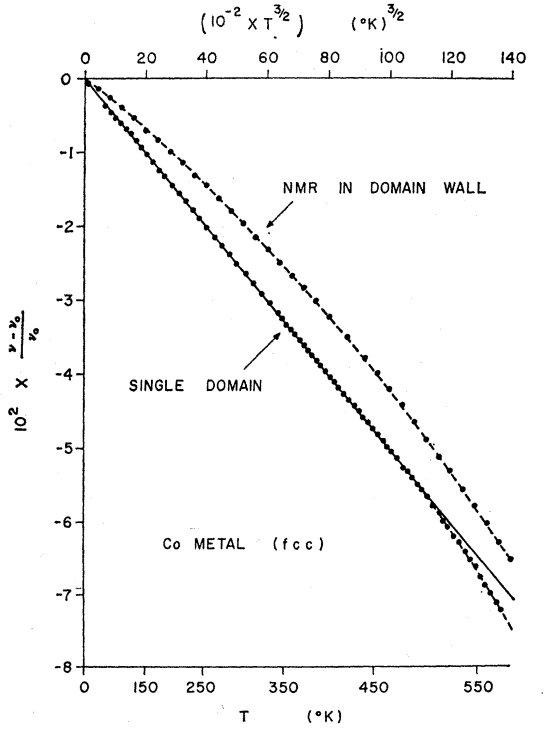

FIG. 4. Normalized fractional decrease with temperature of the Co^{59}-NMR frequencies in single-domain particles (this work) and in domain walls [after Jaccarino (Ref. 3)].

increasing temperature than previously found in multidomain material. This is not in the direction anticipated from the previous theoretical work of Suhl and Winter,[4,5] who predicted a more rapid decrease in walls than in domains.

A detailed interpretation of the present results and a discussion of NMR hyperfine field studies in ferromagnets are in progress, and will be published in a separate paper.

[4] H. Suhl, Bull. Am. Phys. Soc. **5**, 175 (1960).
[5] J. M. Winter, Phys. Rev. **124**, 452 (1961).

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Three-Dimensional Magnetic Model with Classical Spins of High Dimensionality

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A magnetic model with ν-dimensional classical spins on an s-dimensional lattice has been analyzed by Stanley. He demonstrates that the term proportional to ν in the free energy is that given by a spherical-model assumption. Further terms are $O(\nu^0)$. We show, for a three-dimensional lattice, that even for large ν this next-order term makes a contribution which eventually dominates as the critical point is approached, and below the transition. A field-theoretic formulation of the Ising model ($\nu=1$) is modified to obtain series developments in ν^{-1} of the system's properties, but near the critical point these series may not be used directly. The difficulties near the critical point examined here go beyond the context of the model.

I. INTRODUCTION

RECENTLY, Stanley[1] has considered the properties of a system of ν-dimensional classical spins, situated at the sites of an s-dimensional lattice. In particular, he arrives at the conclusion that as the dimensionality ν of the spin vectors becomes infinite, the thermodynamic properties become those of the corresponding spherical model[2] for a fixed $T>T_c$. We shall demonstrate in this paper that for three-dimensional lattices his argument does not apply below the critical transition. Moreover, for any finite ν there exists a region above the transition temperature for which the spherical-model terms are not dominant. Thus the limit of approaching the critical point and passing to $\nu\to\infty$ may not be interchanged. The possibility that this may occur was recognized in Stanley's paper.

We begin with a rapid review of a formalism useful for consideration of this problem. It is next demonstrated that as the critical point is approached from above, the terms of $O(\nu)$ are dominated by terms of $O(\nu^0)$. A more complete analysis of the problem for large, but finite, ν may be obtained by a simple extension of recent work of the author.[3] In particular, one can obtain a Feynman-diagram theory that is ordered in $1/\nu$. The diagrammatic development cannot be directly utilized near the critical point. How to cure this difficulty remains one of the great mysteries of theoretical physics.

II. FORMULATION

Consider the system described by the Hamiltonian[1]

$$H=-\tfrac{1}{2}J\sum_{i,j=1}^{N}v_{ij}\mathbf{S}_i\cdot\mathbf{S}_j. \tag{2.1}$$

The sum is over sites of a lattice, which in this paper we take as three-dimensional simple cubic. The ν-dimensional spins have magnitude $\nu^{1/2}$, i.e., $|\mathbf{S}_j|^2=\nu$. By increasing the magnitude of the spin vectors as ν is increased, the transition temperature is kept finite for $\nu\to\infty$. (One can return to a model where the ground-state energy is independent of ν by allowing J to be inversely proportional to ν.)

The normalized partition function is

$$Q=Z(\beta)/Z(0), \tag{2.2}$$

[1] H. E. Stanley, Phys. Rev. **176**, 718 (1968); Phys. Rev. Letters **20**, 589 (1968).
[2] T. H. Berlin and M. Kac, Phys. Rev. **86**, 821 (1952).
[3] E. Helfand, Phys. Rev. **180**, 600 (1969). This paper will be referred to as I.