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Nuclear Magnetic Resonance Spectrum of Co^{59} in Metallic Cobalt Powders*

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The nuclear magnetic resonance spectrum of Co^{59} in metallic powders is presented. This spectrum contains three lines in addition to the already well-known line of Co^{59} in face-centered cubic cobalt (213.1 Mc/sec at 25°C). The other lines are higher in frequency, the highest located 10.0 Mc/sec above the fcc resonance and is much less intense than the fcc. This highest lying resonance is identified to be due to Co^{59} nuclei in hexagonal close-packed cobalt, and we qualitatively account for the lower intensity by examining the effect on the resonance of the nuclear quadrupole moment in a noncubic environment.

We have been examining the nuclear magnetic resonance (NMR) of Co^{59} in finely divided cobalt metal samples. The spectrum contains several lines in addition to the already well-known nuclear resonance of fcc cobalt. The method of observation was similar to that described by Gossard and Portis[1,2] who first observed the resonance for fcc cobalt. The transmission of a frequency-modulated signal through a coaxial line, packed with the powder sample, is displayed on a cathode ray tube. The resonance absorption modifies the transmission when the frequency corresponds to the nuclear resonant frequency. For some powder samples, the oxide coating[3] on the individual particles was sufficient to provide the requisite electrical insulation; in other cases the particles were wax coated by wetting the powders with a solution of paraffin wax in benzene and drying under vacuum. The relative proportions of cubic and hexagonal phases in the powder samples were determined from x-ray patterns measured with a proportional counter spectrometer and Cr K_α radiation.

The NMR traces obtained with a commercially available sample of cobalt[4] at 300°K and 77°K are shown in Figs. 1(a) and (b), respectively. Part (c) of the figure is an index to prominent parts of the spectrum. The frequencies 1 and 2 associated with the main resonance are approximately 0.5 Mc/sec lower than those reported by Portis and Gossard.[2] However, this difference depends upon frequency sweep rate; for very slow sweep rates there is no discrepancy. We note that the line shape also depends upon sweep rate.

The following observations established that the lowest resonance (frequencies 1 and 2) and the highest resonance (frequencies 5 and 6) are to be associated with the fcc and hcp phases, respectively. Figure 2(a) was obtained with a different sample[5] of cobalt powder than that used for Fig. 1. X-ray analysis showed that the ratio of hcp/fcc for the sample of Fig. 2 was 0.19,

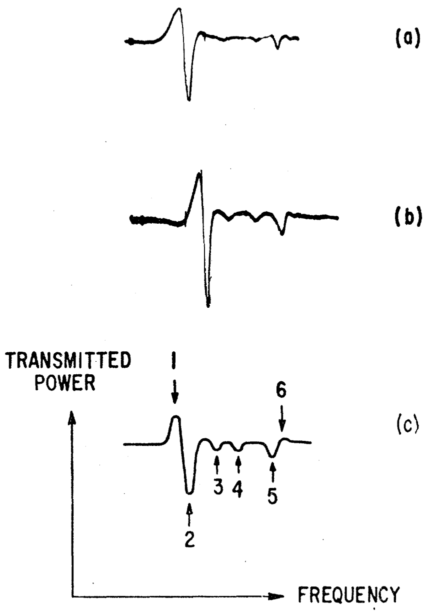

FIG. 1. The nuclear resonance spectrum of cobalt in metallic powders (Matheson, Coleman, and Bell −325 mesh). The figure displays transmitted power vs frequency. The peak to peak variation of the largest signal is 5% of the average transmitted power. Curve (a) is the spectrum at room temperature (300°K); (b) is the spectrum at liquid nitrogen temperature (77°K); (c) is the index to the frequencies tabulated below.

Position	Frequency (Mc/sec) 300°K	77°K
1	211.8_4	215.4_0
2	212.9_7	216.8_3
3	215.4_3	219.8_7
4	218.1_7	223.3_0
5	220.8_0	226.8_7
6	221.9_9	227.9_3

We note without explanation that the shift in resonance frequencies between 300°K and 77°K is linear with frequency.

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[1] A. C. Gossard and A. M. Portis, Phys. Rev. Letters **3**, 164 (1959).

[2] A. M. Portis and A. C. Gossard, Suppl. J. Appl. Phys. **31**, 205 (1960).

[3] The spectra of a powder sample before and after removal of the oxide by heating in a current of dry hydrogen were identical.

[4] Obtained from Matheson, Coleman, and Bell (−325 mesh).

[5] Fisher Scientific Company.

whereas for the powder sample of Fig. 1, the ratio was 1.38. The spectrum of MCB powder, taken with identical apparatus settings, is included for comparison in Fig. 2(b). The reduction of the hcp/fcc ratio is accompanied by a decrease in the intensity of the highest frequency resonance.

To confirm the identification of the NMR resonances, the relative proportion of hcp phase in the MCB cobalt was increased by cold-working the powder.[6] The MCB powder was compressed at 80 000 psi into briquettes which were then powered and annealed for two hours at 300°C; the spectrum in Fig. 3(b) was then obtained. The decreased signal intensity required a higher gain setting than the previous data. A trace of the untreated MCB powder, 3(a), is included for comparison. The intensity of the highest frequency resonance has increased relative to the lowest frequency resonance. The hcp/fcc ratio for the cold-worked cobalt has increased to 4.9. We, therefore, conclude from the data presented here that the lower and higher frequency resonances are associated with the fcc and hcp phases of cobalt, respectively. We understand[7] that Y. Koi (Tokushima University) and W. Hardy (IBM Laboratories, Owego, New York) have both observed a second resonance very similar to that we report here as associated with the hcp phase.

In considering the relative intensities of the resonances of the fcc and hcp phases and allowing for the x-ray determined volume fractions of these constituents, we note that the hcp resonance is weaker by almost an order of magnitude than that of the fcc phase. We believe that the relative weakness of the hcp resonance derives from the interaction of the nuclear quadrupole moment of the Co^{59} nucleus with the noncubic crystalline field of the hcp phase. In a crystalline electric field of cubic symmetry the Co^{59} nucleus ($I=\frac{7}{2}$), subject to a strong hyperfine field, H_{eff}, has $(2I+1)$ distinct energy levels which are equally spaced by $\Delta=g_N\beta_N H_{\mathrm{eff}}$. However, in a noncubic crystalline field, there is an electric field gradient at the nucleus that interacts with the nuclear quadrupole moment. The quadrupolar interaction shifts the energy levels and only the transition $-\frac{1}{2}\rightarrow+\frac{1}{2}$ is still given by Δ.[8] The other transitions are shifted to higher or lower frequencies dependent upon the relative orientation of the crystalline field gradient and the effective magnetic field. The order of magnitude of these shifts may be as much as 20 Mc/sec, which value is observed for the Co nucleus in CoF_2.[9] We recognize that this comparison of electric field gradients between CoF_2 and cobalt metal is by no means justified, and we quote the value here simply for illustration. In addition to the shift of the energy levels caused by the noncubic crystalline environment, the relative orientations of the local effective hyperfine field are randomized by the domain walls that "drive" the resonance. Within the domain walls the effective magnetic field scans all directions between the positive and negative c axes and this randomization broadens all but the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ resonance line because of the anisotropy of the energy levels. Consideration of the transition probabilities shows that the relative intensity of absorption from just the $-\frac{1}{2}\rightarrow+\frac{1}{2}$ transition is 4/21. We thus expect that the hcp cobalt resonance intensity should be, on the above considerations, 20% of the intensity associated with an equal volume of fcc cobalt.

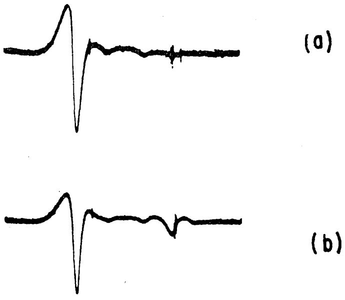

FIG. 2. (a) Room-temperature NMR spectrum of a fine grained powder sample of metallic cobalt (Fisher Scientific Company) which has an hcp/fcc ratio of 0.19 as determined by x-ray analysis. (b) Room-temperature NMR spectrum of the MCB sample in which the hcp/fcc ratio is 1.38.

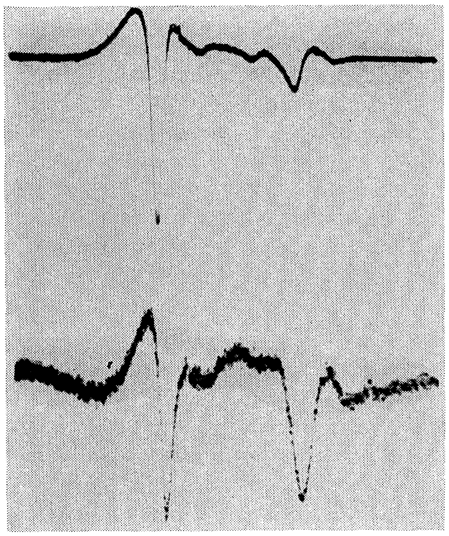

FIG. 3. (a) Room-temperature NMR spectrum of an MCB sample. (b) NMR spectrum of the same sample after a deformation and heat treatment that converted sufficient fcc to hcp to give an x-ray-determined hcp/fcc ratio of 4.9. Part (a) is upper trace of the figure, (b) lower.

From the relative positions in frequency of the res-

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[6] C. Houska, V. Averback, and M. Cohen, Acta Met. **8**, 82 (1960).

[7] A. Portis (private communication).

[8] This statement is correct only to first-order perturbations. In the second-order treatment there is an additional shift, but more important, there is also a broadening of the levels. For an analogous effect in electron spin resonance, see B. Bleaney, Phil Mag. **42**, 441 (1951).

[9] V. Jaccarino, Phys. Rev. Letters **2**, 163 (1959).

onances, we note that $H_{\rm eff}$ for the hcp phase is 5% higher than for the fcc phase. The various contributions to $H_{\rm eff}$ have been discussed,[2] and it is clear that small changes in the contributing terms could account for the magnitude of the difference observed. A proper calculation of this point seems lacking to date.

The origin of the smaller resonances at frequencies 3 and 4 has not yet been determined, but it is tentatively suggested that they are associated with stacking faults. Both growth and deformation faults are observed in hexagonal cobalt.[6] Growth faults are sequences of three planes, and deformation faults are sequences of four planes of cubic close packing within the hexagonal phase. If the identification of the smaller resonances with faulted material is correct, the resonance at frequency 3, nearer the fcc absorption, probably is associated with deformation faults; whereas, the resonance at frequency 4, nearer the hexagonal absorption line, is associated with growth faults. These possibilities are currently being investigated.

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Isotope Effect in Superconducting Lead*

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The present work is a continuation of earlier measurements of the difference in critical fields of superconducting Pb specimens with various isotopic masses. The isotope samples have been repurified and the low-temperature behavior is now more fully understood. The results near T_c are consistent with the relation $T_c = \text{const}\times M^p$, where M is the average isotopic mass, and yield a value $p = -0.478 \pm 0.014$. The measurements at lower temperatures confirm the similarity principle to within approximately 0.1% and indicate that γ, the coefficient in the normal electronic specific heat, is independent of isotopic mass to a similar accuracy.

INTRODUCTION

THE isotope effect for a superconductor is usually discussed in terms of the shift in critical temperature T, resulting from variation in the average isotopic mass, M. Both theory[1] and experiment[2] agree in the result that $T_c = \text{const}\times M^p$ which is valid for isotopic mixtures of a given superconducting element. A value of p close to -0.5 is well confirmed for all elements for which measurements have been made.[2,3]

Study of the isotopic shift in the critical field H, at temperatures below T_c presents special problems in the case of lead. As shown recently,[4,5] this element is particularly susceptible to a type of hysteresis in the magnetic transition which obscures the determination of H_c and complicates the measurement of the rather small isotopic shift.[3]

The results described here were obtained after repurification of the same isotopically enriched Pb specimens whose properties have been described in earlier reports,[3,4] together with one new sample. Some of the ambiguities of the earlier data have now been removed.

EXPERIMENTAL

The apparatus and techniques were largely those of the earlier papers to which the reader is referred for details.[3,4] Ballistic induction measurements were made over the range from T_c (7.175°K) to 1.2°K. Because as many as five specimens were in the cryostat simultaneously, correction was made for the field interference effect (i.e., the distortion of the applied field at one specimen caused by the presence of other superconducting specimens in the vicinity).[3] This could be done exactly if the magnetic state of the other specimens was well known. However, there was some indication of flux trapping by two of the specimens which could not be precisely determined by the present method and so led to an uncertainty in this correction.[6] The best available estimate of the extent of flux trapping came from a com-

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[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); hereafter referred to as BCS.

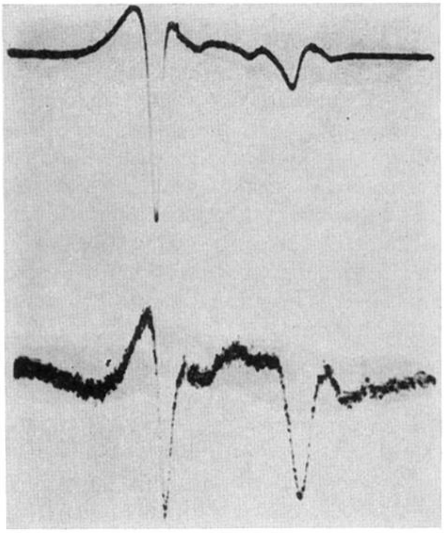
[2] B. Serin, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 142.

[3] R. R. Hake, D. E. Mapother, and D. L. Decker, Phys. Rev. **112**, 1522 (1958).

[4] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. **112**, 1888 (1958).

[5] R. W. Shaw and D. E. Mapother, Phys. Rev. **118**, 1474 (1960).

[6] Flux trapping here refers to that flux remaining in the sample when the applied field is lowered to roughly $0.8H_c$, the lowest field normally reached between transitions in these measurements.



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