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Nuclear Magnetic Resonance in Ferromagnetic Metals and Alloys

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Firstly, measurements of the NMR frequency of the Co^{59} in hexagonal and cubic cobalt have been made as a function of temperature up to 956°K and 1157°K respectively. The difference in the resonance frequencies in hexagonal and cubic cobalt remains constant at a value of 3.5 Mc/sec above the transition temperature 723°K as is expected from Keffer's interpretation of this difference. Secondly, the internal fields at the Cu dissolved in iron and cubic cobalt have been measured by means of NMR. The value of the field at the Cu in iron is 212.7 koe at 0°C and that in cobalt is 157.5 koe at 9°C. The pressure dependence of the field H_i at the Cu in iron has also been measured at 0°C with the result that the $d\ln H_i/dp$ is -3.0×10^{-7} $(kg/cm^2)^{-1}$. A brief discussion on mechanisms possible as the source of the field is given.

We wish to report (1) the temperature dependence of the Co^{59} NMR frequency in hexagonal and cubic cobalt at higher temperatures and (2) the results of the NMR experiments of the Cu dissolved in iron and cobalt.

(1) NMR in hexagonal and cubic cobalt

The Co^{59} NMR frequency in hexagonal cobalt is 10.8 Mc/sec higher at O°K and falls off more rapidly with increasing temperature than that in cubic cobalt[1]. According to Keffer[2], these differences are due to the fact that the c/a ratio in hexagonal cobalt is slightly deviated from the ideal value at lower temperatures and becomes gradually ideal as the temperature approaches the transition temperature 723°K. Portis[3] suggested that the difference in the frequencies should remain constant at higher temperatures. In accordance with his suggestion NMR measurements in hexagonal and cubic cobalt were made up to 956°K and 1157°K respectively. The result is as expected and is shown in Fig. 1. The difference remains constant at a value of about 3.5 Mc/sec above the transition temperature.

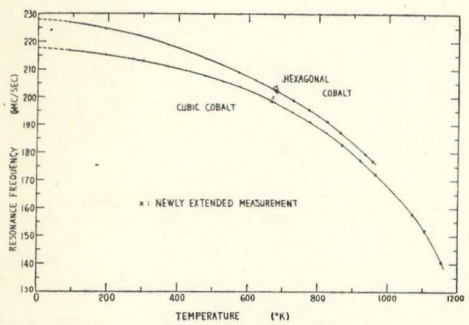

Fig. 1. The temperature dependence of the Co^{59} NMR frequency in hexagonal and cubic cobalt.

(2) NMR of the Cu dissolved in iron and cubic cobalt

The internal fields at the Cu nucleus in iron and cubic cobalt have been measured by means of NMR in zero external field. The pressure dependence of the former has also been measured at O°C in the pressure range 1 to 8000 kg/cm². The samples were powders of dilute alloys prepared from high purity metals in an induction furnace. Each alloy contains about 1% copper. A frequency-modulated marginal oscillator was used for detecting the resonance and the resonance signal was displayed on an oscilloscope.

The results of the internal field measurements are shown in Table I. The data for pure iron[4] and cubic cobalt[5] are included in it for comparison. Unfortunately the sign of the field is unable to be determined ex-

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Table I. The internal fields at the Cu nucleus in iron and cobalt. The data for pure iron and cobalt are included for comparison.

Nucleus	Temperature °C	Resonance frequency Mc/sec	Internal field koe
Cu^{63} in Fe	0	240.0	212.7
Cu^{65} in Fe		257.1	
Cu^{63} in Co	9	177.8	157.5
Cu^{65} in Co		190.7	
Fe^{57} in Fe	0	46.65	330.5
Co^{59} in Co	0	213.2	213.5

Table II. The pressure dependence of the internal field at the Cu nucleus in iron at 0°C. The data for C^{59} and Fe^{57} are also included for comparison.

Nucleus	$d\ln H_i/dp$ $(kg/cm^2)^{-1}$
Cu^{63} in Fe	-3.0×10^{-7}
Co^{59} in Fe	$+1.6\times10^{-7}$
Fe^{57} in Fe	-1.6×10^{-7}

perimentally. Table II shows the pressure dependence of the field H_i at the Cu^{63} in iron along with those at the Co^{59} in iron[6] and Fe^{57} in iron[7]. The resonance frequency of the Cu^{63} decreases linearly with increasing pressure. The followings are to be noted: (a) The internal fields at the Cu in iron and cobalt are comparable in magnitude with the fields in pure iron and cobalt. (b) The ratio of the fields at the Cu in iron and cobalt is nearly equal to that of the saturation magnitizations of iron and cobalt. (c) The pressure dependence of the field at the Cu in iron is more negative than that at the Fe^{57} in iron.

Now we wish to discuss the origin of the field. According to Marshall[8], the internal field in iron group ferromagnets arises mainly from the contact interactions of the nucleus with the 4*s* electrons and with the inner core electrons. The contribution from the 4*s* electrons consists of two parts. The first part is due to the 4*s* conduction electrons polarized by the spins of the 3*d* electrons, and the second part is due to some mixing of the 4*s* wave function into 3*d* band. Both parts produce a positive field, *i.e.*, a field parallel to the direction of the magnetization. On the other hand, the inner core *s* electrons polarized by the spin of the 3*d* electrons produce a negative field. The actual field is of negative sign. In the case of a dilute alloy of copper in iron or cobalt, things are somewhat different since copper is basically nonmagnetic. The following mechanisms[9] are possible as the source of the field at the Cu nucleus in iron or cobalt: (I) The 4*s* conduction electrons polarized by the spins of the 3*d* electrons of the solvent atoms produce a field at the Cu nucleus through contact interaction. (II) The Cu atom loses some of its 3*d* electrons when dissolved in iron or cobalt[10] and the resulting spin of the 3*d* shell produces a field through the same mechanisms as in pure ferromagnets. (III) The 3*d* spins of ferromagnetic atoms neighboring to a Cu atom can produce a field at the Cu nucleus through several mechanisms other than (I) and (II). Any one of possible mechanisms we refer to as the third mechanism. One mechanism is the polarization of the inner core *s* electrons caused by the 3*d* spins of neighboring atoms directly[11], or indirectly through the medium of the 3*d* shell of the Cu atom. Another mechanism is a possible mixing of the *s* wave function of the Cu into the 3*d* wave function of the neighboring atoms.

Our results, however, are not likely to be explained from any single mechanism. The first mechanism is the simplest, but the values of the observed fields are too large to be explained from it. It seems that the pressure dependence is not easily explained from the second mechanism. If this mechanism is the main source of the field at the Cu nucleus, we may expect that the $d\ln H_i/dp$ for the field at the Cu is positive or at least equal to that at the Fe^{57}. The observed pressure dependence is, however, in disaccordance with this expectation. Lastly let us assume that the third mechanism is the main source of the field. Then the same mechanism will play an important role also in pure ferromagnets. This makes it difficult to understand the above mentioned experimental result (a). In addition, if the assumption is true, the presence of a Cu atom in Co metal will result in a large change in the field at the Co nuclei neighboring to the Cu

atom. The observed change is, however, less than 1%[12]. (We have assumed that the satellite of the Co^{59} resonance line in the Cu-Co alloy is due to the Co nuclei neighboring to the Cu atom.) Thus it seems to be difficult to account for the present data in terms of a single mechanism, though some of the difficulties mentioned above are not serious. It is likely that a combination of these mechanisms is responsible for the field.

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9 After this paper had been nearly completed, we were able to see a preprint of the following article: R. E. Watson and J. Freeman: Phys. Rev. (to be published). They suggest almost the same mechanisms as ours except our second mechanism. We are grateful to Dr. Freeman for the preprint.
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DISCUSSION

W. MARSHALL: It would be valuable to extend your measurements to Cu in Ni, particularly if you could measure the sign of the field, because Mössbauer experiments by Boyle on Sn in Fe, Co and Ni show that the field is negative in Fe and Co and positive in Ni. It would be valuable to know if the same were true for Cu impurity.

A. M. PORTIS: The constant of the splitting of the hexagonal and cubic resonances at high temperatures suggests three possibilities. Either (1) the c/a ratio does not approach the ideal value or (2) the atomic volume does not approach that of the cubic phase or (3) there is a systematic shift associated with the ideal hexagonal structure. High temperature structure studies of the hexagonal phase would be valuable in resolving this problem.

W. MARSHALL: At Harwell, G. Perlow has performed a Mössbauer experiment on a Co single crystal. Using a strong field he is able to orient the magnetization parallel and perpendicular to the c axis and in this way is able to measure the dipolar contribution to the hyperfine field for Fe^{57} in Co, admittedly not quite the same as Co in Co. He finds the effect to be very small and my recollection is that he puts an upper limit on the effect of the order of magnitude of the 4 Mc/s observed in this experiment. These experiments are continuing and a better result should be available soon. It should also be remembered that the saturation magnetization of face centred cubic cobalt is slightly higher than that of hexagonal cobalt. This gives an effect of opposite sign to that observed for the difference in hyperfine field between the two forms of cobalt.