MAGNETIC BEHAVIOR OF VERY DILUTE Co IN Au †

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We have used nuclear orientation to measure the internal magnetic field at nuclei of Co in dilute Au(Co) alloys for various values of the applied magnetic field. We find $H_{\mathrm{internal}}/H_{\mathrm{applied}} = 1.29 \pm 0.11$ at high fields, indicating a relatively large magnetic moment on the Co.

We present here the first measurement of the hyperfine interaction of Co in Au and Cu at very low concentration and temperature. Recent work indicates that V in Au[1] and Co in Cu[2] and Au[3] are essentially "nonmagnetic" when dilute, whereas in clusters V and Co interact in such a way that they behave more or less as if they were in pure V or Co metal, respectively. (We use "magnetic" and "nonmagnetic" in a comparative sense to describe whether or not the Knight shift exceeds 5-10%. This use would roughly correspond to that of Tournier and Blandin[2] but not of Narath and Gossard.[1]) Our results support the argument on Co in Cu in a field of 40 kG near $T = 0$ K.

Cr, Mn, and Fe are known to show Kondo behavior in Cu and Au hosts.[4] Experiments have been performed on these with the impurity level below 100 ppm. For Co and V, the experiments have required concentrations above 0.1% because of the low impurity susceptibility. As the concentration is raised above 1%, the magnetic moment per atom increases for Co impurities and the Knight shift changes from negative to positive for V impurities. It has been concluded that in the low-concentration limit V and Co will be nonmagnetic.[1-3] This is an important point, as these two ions seem to be on the border of the transition from magnetic to nonmagnetic behavior in these hosts.

Nuclear orientation is a particularly useful technique for the study of Mn and Co as very low concentrations can be used, 10^{-9} and 10^{-6}, respectively. The temperature is limited to the region below 50 mK, which should be in the $T = 0$ limit for Co impurities. We measured the γ-ray anisotropy of ^{60}Co in various applied fields and computed from this the internal field at the nucleus. This in turn is proportional to the local moment of the ion, so one is basically measuring that moment. The major difficulty is establishing a numerical relation between the hyperfine field and the electronic moment. Since we could neither saturate the Co moment in the available fields nor measure the moment directly, this relationship has not been determined.

Two samples of ~7 μCi of 5.2-yr ^{60}Co in gold were prepared by evaporating a HCl solution of ^{60}Co onto a 99.999%-Au foil and then melting. Sample No. 1 was melted in a 5% H_2, 95% Ar atmosphere and sample No. 2 in a 15% H_2, 85% N_2 atmosphere. The alloys were then flattened to 0.010 in. and annealed, sample No. 1 at 700°C for 20 h and sample No. 2 at 950°C for 2 h. The Co content, calculated from the specific activity of the ^{60}Co, was less than 5 ppm. The resistivity ratios, ρ(300 K):ρ(4.2 K), were greater than 200:1 indicating a total magnetic impurity level of less than 20 ppm. A foil of the alloy and a thermometer (^{54}Mn in Cu) were soldered to the copper fin assembly which served as a heat link to a salt pill consisting of a cerium magnesium nitrate–glycerin slurry. The sample was cooled to 0.008 K by adiabatic demagnetization from 0.3 K, and the temperature determined from the anisotropy of the 840-keV γ ray of the ^{54}Mn in Cu.[5,6] A Ge(Li) detector was used to measure the γ-ray intensities. $W(0)$, the γ-ray intensity measured along the axis defined by the applied field and normalized to the high-temperature (0.3 K) intensity, was determined as a function of the applied magnetic field, H_{app}. Results quoted here are the statistical average of the data on these two samples. More data were taken on sample No. 2 and it alone is shown in Fig. 1. A third sample, remelted several times during preparation, was observed using scintillation crystals. The results are consistent with those quoted here but are less reliable than those for the other two taken with the Ge(Li) detector and so are not averaged in. All errors have been calculated assuming only statistical variations.

The results for $W(0)$ are shown in Fig. 1 for the three values of applied field used. The applied field values are known to better than ±3%. The magnetic field at the nucleus, $H_{\mathrm{int}} = H_{\mathrm{app}} \pm H_{\mathrm{hf}}$, was obtained by a least-squares fit of the data by the expression

$$W(0) = 1 + a_2 B_2(H_{\mathrm{int}}/T) + a_4 B_4(H_{\mathrm{int}}/T), \qquad (1)$$

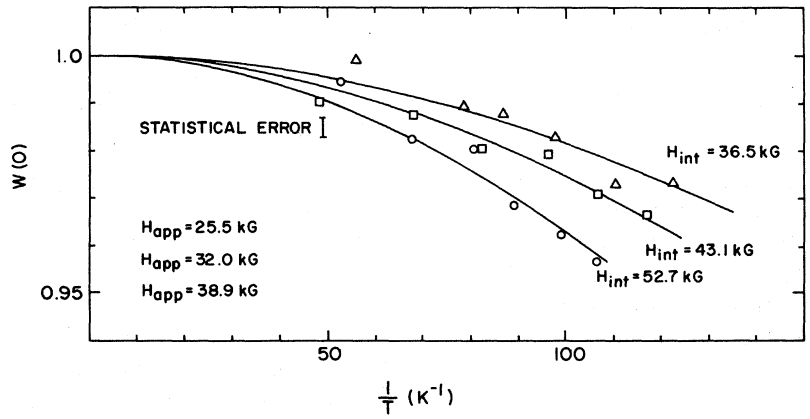

FIG. 1. Gamma ray anisotropy of oriented ^{60}Co in gold as a function of reciprocal temperature for various values of H_{app} for sample No. 2. The curves are least-squares fits to the experimental data and were calculated using the values of H_{int} shown.

where the a's are constants calculated from the known decay parameters of ^{60}Co and the detection angle and the B's are functions of the nuclear Zeeman-level populations in field H_{int} at temperature T.[7] We obtain $H_{int}=(1.29\pm0.11)H_{app}$ for Co in Au in magnetic fields greater than 20 kG. Our results are consistent with the null results of Cameron et al.,[8] who used a maximum field of 15 kG and $1/T$ of 70 K^{-1} at which the anistropy would have been only 0.3%.

In Fig. 2 we plot H_{int} vs H_{app} for Co in Au. Two important features stand out: H_{int} (1) is large and (2) linearly extrapolates to nearly zero at $H_{app}=0$. (The intercept of a least-squares-fit straight line is $H_{int}=3.2\pm3.5$ kG. The slope gives $H_{hf}/H_{app}=2.29\pm0.11$, assuming the hyperfine field is negative, or 0.29 ± 0.11, assuming the field is positive.)

There are three alternative interpretations of these results, any one of which is very unexpected:

(1) If the hyperfine field is negative, i.e., $H_{int}=H_{app}-H_{hf}$, and Hildebrand's data[9] at 0.4% Co are used for the susceptibility and effective moment of the cobalt impurity (giving a moment of $0.074\mu_B$ at 40 kG and $T=0$), we obtain $H_{hf}/\langle\mu\rangle=(1260\text{ kG})/\mu_B$! This is compared with (131 kG)/μ_B for ^{59}Co in Co metal. Also, $H_{sat}=5750$ kG compared with 225 kG in Co metal.

(2) If the hyperfine field is positive and we again use Hildebrand's numbers, then $H_{hf}/\langle\mu\rangle=(182\text{ kG})/\mu_B$, still somewhat high but reasonable.

(3) If the hyperfine field is "normal" [say (130 kG)/μ_B and negative] and $\mu_{eff}\simeq4.5\mu_B$, then the linear increase of magnetization with field at these high fields is typical of a Kondo-type system with $T_{Kondo}=32$ K, where we have used

$$\chi\approx(\mu_{eff})^2/3kT_K \tag{2}$$

and

$$H_{hf}/H_{sat}=M/M_{sat}. \tag{3}$$

If μ_{eff} (and also therefore H_{sat}) were half this value, then $T_K\cong(32\text{ K})/2^3\cong4$ K. In this case we should see evidence of magnetic saturation in the

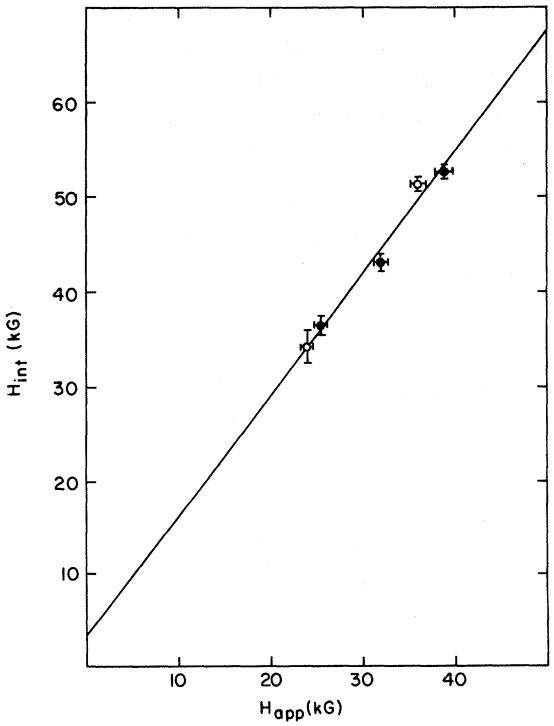

FIG. 2. H_{int} vs H_{app}. The line drawn is a least-squares fit to the data and is given by H_{int}(kG) = (3.2 $\pm$3.5) + (1.29 $\pm$0.11)H_{app}(kG). Open circles, sample No. 1; filled circles, sample No. 2.

data. We do not feel that the data are sufficiently precise to make any deductions about this matter at this time.

Of these three possibilities the first two, either the enormously large hyperfine coupling required in (1) or the positive coupling in (2), contradict what is presently known about the hyperfine structure of the iron-series elements. In insulators the saturation hyperfine field of these elements may be as high as 500-700 kG, in metals typically 200-300 kG.[10] Thus the field required in (1) is at least an order of magnitude higher than any known at present. Cobalt in palladium apparently has a positive hyperfine coupling.[8] This is, however, a giant-moment system and a negative hf coupling is expected in all noble-element hosts. At high concentrations V in Au shows a positive Knight shift, but this becomes negative below 1% V concentration, the positive shift being due to V-V interaction effects.[1] Our 5-ppm concentration is certainly in the dilute limit and Co might be expected to behave somewhat like V, just as Cr and Fe are similar.

It would also appear that (3) contradicts all previous work on Co in Au. However, if the Kondo temperature is indeed about 25 K, then most previous work has been done at concentrations somewhat too high; for at $T_K \approx 25$ K, the concentration of the magnetic impurity should be kept below 0.1% in order to preclude interaction effects. Incremental resistivity measurements in the dilute limit (<0.1%) have given mixed results. The work of van den Berg, van Herk, and Knook[11] showed virtually no low temperature minimum, while that of Loram, Ford, and Whall[12] showed a pronounced minimum at 13 K, though not of the familiar Fe in Cu form.[4] Also, the Kondo temperature of a given element is typically lower in Au than in Cu. For example, Mn in Cu shows $T_K = 0.064 \pm 0.002$ K,[6] while Mn in Au behaves like a free ion of spin $\frac{5}{2}$ to below 0.020 K.[13] Similarly, the Kondo temperature for iron in copper is much higher than for iron in gold.[14] If we assume a positive saturation field of 300 kG and $\mu_{eff} = 4.5\mu_B$, then $T_K \approx 120$ K.

Finally, we are studying Co in a series of Au-Cu alloys as well as Au with a high Co concentration. For Co in pure Cu we obtain $H_{int} = (5.7 \pm 3.9) + (0.92 \pm 0.12)H_{app}$. Clearly the Co in Cu is "nonmagnetic." We shall publish these studies as soom as they are completed.

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