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Test for Band Ferromagnetism in hcp Cobalt: Knight Shift in the Ferromagnetic Phase of Cobalt

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A high-field Knight-shift measuremnt in a single crystal of hcp cobalt, $K=0.0186$, is used to derive the spin susceptibility $\chi^p = 71\times10^{-6}$ emu/mole and the orbital susceptibility $\chi_{vv} = 202\times10^{-6}$ emu/mole. Comparing the results with predictions of the ferromagnetic band model, we conclude that hcp cobalt is a weak itinerant-electron ferromagnet.

It is now believed on general grounds[1] that the ferromagnetic 3*d* metals—iron, nickel, and cobalt—are itinerant-electron ferromagnets. However, while models of band ferromagnetism could account for some observations in cubic iron and nickel,[2,3] so far very little conclusive evidence was presented connecting properties of hcp cobalt with band ferromagnetism.[4] In the present Letter a high-field "Knight-shift" study in a single crystal of hcp cobalt, in the ferromagnetic phase, is described and the results utilized to test in a critical manner the predictions of the band model of ferromagnetism concerning the spin susceptibility, χ^p, in cobalt. Simultaneously, an *experimental* value of the orbital susceptibility, χ_{vv}, in the ferromagnetic phase of hcp cobalt is determined.

First, a brief review of existing information relevant to the present study. As is well known,[5] a prediction of the ferromagnetic band model can be tested directly by measuring the high-field spin susceptibility χ^p, high field meaning applied magnetic fields well above technical saturation. The model prediction[4] in the low-temperature limit is

$$\chi^p = 4\mu_B{}^2/\{[N_{\rm min}(E_F)]^{-1} + [N_{\rm maj}(E_F)]^{-1} - 2I\}. \quad (1)$$

Based on results of two independent pioneering band-structure calculations[6,7] available at the time it was concluded[4] that hcp cobalt is a so-called "strong" itinerant-electron ferromagnet, i.e., one in which the majority-spin sub-band is fully occupied. As a result, in accordance with Eq. (1), only a small χ^p value [$(20-25)\times10^{-6}$ emu/mole] was predicted. In a more recent band calculation,[8] based on hcp interpolation schemes and claiming improved accuracy, it is found that neither sub-band is yet fully occupied, delineating hcp cobalt as a "weak" itinerant-electron ferromagnet with χ^p being 3 times larger than the predictions based on Refs. 6 and 7. Some time later[9] the *total* high-field susceptibility of hcp cobalt was measured yielding $\chi^{\text{total}} = (265 \pm 2) \times 10^{-6}$ emu/mole, i.e., 10 to 3 times larger than any of the band predictions above for χ^p. χ^{total}, however, contains a large orbital contribution, χ_{vv}, for which so far neither experimental nor theoretical values are available. Following a reasoning that was first suggested by Clogston, Jaccarino, and Yafet,[10] educated guesses for χ_{vv} in cobalt, albeit cubic cobalt, vary between 98×10^{-6} emu/mole[4] and 140×10^{-6} emu/mole.[11] Not knowing any better, subtraction of the above estimates from χ^{total} leaves an apparent "experimental" χ^p that is still 2 to 8 times larger than that predicted by the band models[6-8] mentioned.

To settle the apparent failure of the band model in the present context, it is necessary to determine in an independent experimental measurement either χ^p or χ_{vv}. Such determination is possible by combining results of a high-field Knight-shift measurement with the high-field χ^{total} result. In a way, the procedure to be outlined below is related to the classical studies of K versus χ in the paramagnetic transition metals[10-12] and, when applicable, similar notations will be used. The total high-field susceptibility is a linear sum of individual χ contributions:

$$\chi^{\text{total}} = dm/dH = \tfrac{2}{3}\chi_s^{\,p} + \chi_d^{\,p} + \chi_{\text{dia}} + \chi_{vv}, \qquad (2)$$

where $\chi_s^{\,p}$ and $\chi_d^{\,p}$ are the s- and d-band spin contributions, respectively, and χ_{dia} is the dimagnetic core contribution.

We now define a high-field Knight shift K by

$$K = [(\Delta\nu/\gamma^{59}/2\pi) - \Delta H]/\Delta H \equiv (\gamma_{\text{eff}} - \gamma^{59})/\gamma^{59}, \quad (3)$$

where $\Delta\nu$ is the total frequency change observed for a change ΔH in the externally applied field H, with $H >> DM$, and $\gamma_{\text{eff}}/2\pi = \Delta\nu/\Delta H$. K can be written also as another independent linear combination of the various χ terms,[10-12]

$$K = \alpha_s \chi_s^{\,p} + \alpha_d \chi_d^{\,p} + \alpha_{vv}\chi_{vv}. \qquad (4)$$

Now, by far the largest terms in both Eqs. (2) and (4) are $\chi_d^{\,p}$ and χ_{vv}. Using known semiempirical values or reliable estimates for the other terms, most of which are rather small anyway, the two independent relations, Eqs. (2) and (4), will yield experimental values for both $\chi_d^{\,p}$ and χ_{vv} in terms of K and χ^{total}, from which the desired spin susceptibility $\chi^p = \chi_d^{\,p} + \chi_s^{\,p}$ is determined.

If nothing else, the distribution of demagnetizing fields in a powder sample of Co makes it impossible to determine K in such a sample, and a single crystal is a must. Because a Knight-shift experiment in a technically saturated metallic ferromagnet, let alone in a single-crystal sample, has never been reported previously,[13] some essential details concerning sample handling and experimental setup are described below. The criteria for observing narrow NMR lines in a metallic single-crystal ferromagnet were discussed very recently.[14] According to these criteria, surface roughness of $\delta' \lesssim 10^{-4}$ cm and fractional deviation from sphericity of $\delta/d \lesssim 0.01$ are required to realize NMR linewidth $\Delta W \lesssim 1$ kG in a metallic cobalt sphere. The single crystal of hcp cobalt was grown by zone-melting 99.99% cobalt rod in an electron-beam furnace. A sphere with $d = 0.5$ cm was cut from the rod by spark erosion, ground and polished mechanically with Al_2O_3 powder, electropolished,[15] and finally annealed under H_2 atmosphere at 360°C for 20 h. X-ray analysis following each step confirmed that all of the above steps were indeed necessary to minimize structural damage at the surface of the sphere, an important point if the measurement is to be performed in a well-defined hcp phase. The sphere was then wrapped in a 2×10^{-3}-cm-thick insulating wrap and placed in a few turns of tightly wound copper wire (A.W.G. No. 46) which formed the resonance coil of conventional spin-echo spectrometers. An external field H in the range of 10–70 kG was applied parallel to the crystalline c axis (±1°). The measurements were conducted at 4.2°K by recording directly the echo amplitude as function of H at various fixed radio frequencies. No signal averaging was used and typical line profiles with $\Delta W \sim 1.3$ kG were obtained with a signal-to-noise ratio of ~50 at the center of each line profile, enabling determination of line centers to ±20 G at each frequency. Two spheres were studied, one in each laboratory (circles and squares in Fig. 1), with probable frequency errors of ±1 kHz (circles) and ±20 kHz (squares).[16]

The resulting center field at each frequency is shown in Fig. 1, curve a (left scale), and it is seen that except for the lowest field point, all the points lie on a single linear curve. Figure 1, curve b (right scale) displays the same data points with a modified and greatly enlarged scale to demonstrate the statistical scatter of the data about the linear slope. A linear "best fit" to all but the first two low-field points yields

$$\gamma_{\text{eff}}/2\pi = |d\nu/dH| = 1.0249 \pm 0.0007 \text{ kHz/G}$$

and a "zero-field" frequency $\nu_0 = 225.75 \pm 0.10$ MHz. To determine K, the "bare" gyromagnetic ratio, γ^{59}, is needed. Because of the properties

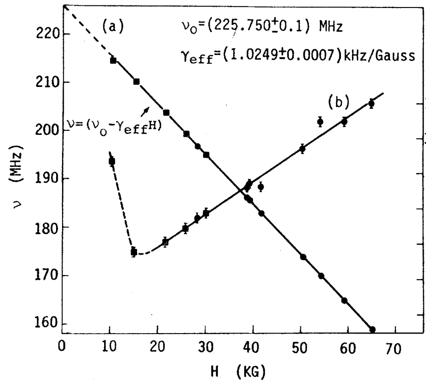

FIG. 1. High-field Knight shift of Co^{59} in ferromagnetic single-crystal hcp Co. Curve a, field versus observed frequency (left scale). Curve b, field versus difference between the observed frequency and the frequency expected for $\gamma_{eff}=\gamma^{59}$ (right scale). Note that for $H<4M/3$ the sphere is no longer technically saturated and ν, even within domains, will not follow the broken part of curve a, but will remain essentially constant.

of cobalt in compounds, no ideal reference compound is available and the value of γ^{59} is not an easy one to come by as is evident from the detailed analysis made a few years ago.[11] Using the best available ratio,[11] $\gamma^{59}/2\pi=1.0054\pm0.002$ kHz/G, we obtain from Eq. (3) the experimental high-field Knight shift of hcp cobalt at 4.2°K,

$$K=(\gamma_{eff}-\gamma^{59})/\gamma^{59}=0.0194\pm0.0025. \quad (5)$$

Using $\chi_{dia}=-6\times10^{-6}$ emu/mole, $\chi_s^p=6.6\times10^{-6}$ emu/mole,[3] and substituting α_s, α_d, and α_{vv} from Ref. 11, we obtain from Eqs. (2) and (4)

$$\chi_d^p=(65\pm25)\times10^{-6}\text{ emu/mole};$$
$$\chi_{vv}=(202\pm25)\times10^{-6}\text{ emu/mole}; \quad (6)$$
$$\chi^p=\chi_d^p+\chi_s^p=(71\pm25)\times10^{-6}\text{ emu/mole}.$$

Most of the probable error in K, and about half the error in χ^p and χ_{vv}, is caused by the uncertainty in γ^{59}, and thus, although with some effort the accuracy in γ_{eff} can be tenfold improved, no such improvement will be realized in the accuracy of χ^p or χ_{vv}.

The experimental value, $\chi^p=71\times10^{-6}$ emu/mole, can now be compared with the ferromagnetic-band-model predictions listed in Table I. The agreement with the value that is calculable from the improved density of states curve[8] (see Fig. 2) is indeed remarkable, particularly so considering that the calculation preceded, by a few years, the measurement. It is therefore concluded that hcp cobalt is a clear case of a

TABLE I. Results of calculations of the state density at the Fermi level (electrons/eV atom), exchange splitting, molecular-field exchange constant, and spin susceptibility.

	Refs. 4,6	Ref. 7	Ref. 8
$N_{min}(E_F)$	1.55	0.88	1.05
$N_{maj}(E_F)$	0.16	0.14	0.45
ΔE (eV)	1.35	1.71	1.13
I (eV)	0.87	1.10	0.72
$\chi_s^p+\chi_d^p$ (10^{-6} emu/mole)	25.1	21.3	74.7

weak itinerant-electron ferromagnet with the Fermi level lying just below the sub-band edge of the majority spins.

Having accomplished the main aim of this Letter, some final comments are called for. A by-product of the study is the relatively accurate, and larger than expected, χ_{vv} value. So far this is the only experimental value available in ferromagnets, and we hope it might lure theorists to attempt calculations based on the detailed band structure of hcp cobalt. The present study may also serve as a feasibility indicator for Knight-shift studies in other metallic ferromagnets. An intriguing possibility is a test of the localized-versus itinerant-electron picture in some of the $4f$ metallic ferromagnets; obvious candidates are hcp Gd metal and cubic $GdAl_2$ intermetallic ferromagnets. Preliminary estimates based on a signal-to-noise ratio for ^{27}Al resonance in single-crystal $GdAl_2$[14] indicate that such experiments are feasible indeed, provided enrichment to ±80% in ^{155}Gd *or* ^{157}Gd is used in the samples.

Technical assistance by A. Gabai in sample

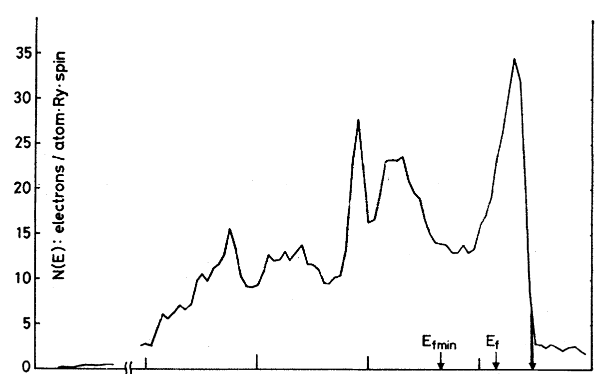

FIG. 2. The theoretical density of states for hcp cobalt (from Ref. 8).

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Configurationally Disordered Spin Systems

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We introduce a model for configurationally disordered spin systems that is exactly solvable in an appropriate spherical approximation for a variety of exchange interactions. For a classical Heisenberg interaction, the solution shows a ferromagnetic transition.

We introduce here a model for configurationally disordered spin systems and show that for exchange interactions of interest the model can be exactly solved in three dimensions in a spherical approximation that is appropriate to it. Our model, which is classical, consists of magnetic solute particles in a nonmagnetic solvent. The solute is in thermal equilibrium with the solvent rather than randomly "frozen in" as an impurity; thus our model appears best suited to describing annealed rather than quenched amorphous magnetic systems. In particular, the simple ferromagnetic version of our model that we solve below seems relevant to annealed cobalt-phosphorus alloys.[1]

In our model the solvent particles are assumed to interact with one another and with the solute particles via a nonmagnetic potential dominated by a highly repulsive core term. For simplicity we shall take the solute-solvent and solvent-solvent interactions to be the hard-sphere terms $\varphi_{ab}{}^H$ and $\varphi_{bb}{}^H$ with diameters R_{ab} and R_{bb}, respectively. Thus for $m=a$ or b, $n=a$ or b,

$$\varphi_{mn}{}^H(12)=\infty \text{ for } r<R_{mn}, \qquad \varphi_{mn}{}^H(12)=0 \text{ for } r>R_{mn}. \tag{1a}$$

Here r is the distance between the centers of particles 1 and 2. The magnetic solute particles will be assumed to interact with one another through a