NMR STUDIES IN PARAMAGNETIC AND FERROMAGNETIC $CrBe_{12}$

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The bulk nature of the magnetization of $CrBe_{12}$ is verified and the paramagnetic Curie temperature of about 50°K confirmed by conventional high-field NMR in the ferromagnetic as well as in the paramagnetic state. The equality of the hyperfine constants in the ferromagnetic and paramagnetic states suggests true ferromagnetic ordering. Significant magnetization density on the Be sites is inferred.

In this Letter, we report the first measurement of hyperfine fields in a ferromagnetic metal by conventional field-modulated, field-swept (fixed-frequency), high-field NMR.[1] Measurements were made on ^9Be in $CrBe_{12}$ as a function of temperature continuously from the paramagnetic state, through the Curie point, into the ferromagnetic state. The difference in magnetic field between the resonance of the reference salt ($BeCl_2$) and of $CrBe_{12}$ is proportional to the frequency used (i.e., it is a Knight shift) well above the Curie point; in the ferromagnetic state, the field difference is approximately frequency independent, and is directly related to the measured magnetization.

The NMR results obtained in $CrBe_{12}$ verify that the ferromagnetism reported[2] for this material is indeed a bulk phenomenon. Furthermore, the resonance results yield an independent estimate of the paramagnetic Curie temperature, θ_p, of about 50°K, in excellent agreement with the earlier macroscopic studies. It is also possible to estimate, from the observed Be hyperfine fields, the presence of a small magnetic moment at the Be sites, oriented antiparallel to the net magnetization (which is presumably associated with a larger moment at Cr sites). The earlier magnetization and susceptibility study yielded a paramagnetic "moment" (P_{eff}) of $2.2\mu_B$/formula unit, and a ferromagnetic saturation moment, M_S, of $0.34\mu_B$/formula unit. A large value of the ratio P_{eff}/M_S such as obtained here is now often[2] taken as one criterion of collective or "itinerant" ferromagnetism.[3]

The ^9Be resonances observed, at a fixed frequency, are shown at some representative temperatures in Fig. 1. These results were obtained using a commercial wide-line nuclear induction spectrometer, operating in the dispersion mode, with 80-Hz magnetic field modulation. The dc magnetic field was swept over the appropriate range centered near 13-15 kG (1 G = 10^{-4} T). A gas-flow Dewar, using either N_2 or He gas, was used for temperatures from 40°K to room temperature. The line shapes are badly distorted by saturation and possible quadrupole effects,[4] and caution must be used in attributing any significance to the observed structural features of the lines, other than the line centers, gross widths, and perhaps any asymmetries. The

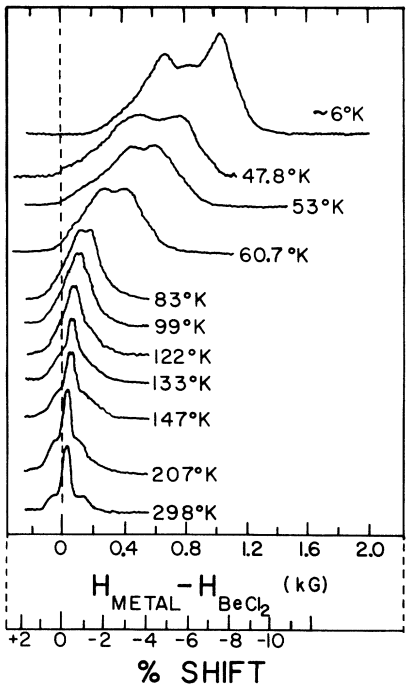

FIG. 1. The dispersion derivatives of the ^9Be NMR line in $CrBe_{12}$ at several temperatures, at 8.000 MHz, and at an applied rf level between about 0.5 to 1 G. The zero of the abscissa is the resonance field for $BeCl_2$ solution (13.37 kG).

shifts of the line centers, and the linewidths, become gradually larger as the temperature is lowered, without any obvious discontinuity at the Curie point.

Assuming Curie-Weiss behavior [i.e., $(K-K_0)\times(T-\theta_p)=\text{const}$] the best fit for the Knight shift, K, in the paramagnetic state yields[5] $K_0=-(0.08\pm0.02)\%$ and $\theta_p=50\pm1$°K. This value of θ_p is in excellent agreement with $\theta_p=49.7$°K reported[2] from susceptibility measurements. Plotting as K vs T, one obtains the hyperbolic solid line displayed in Fig. 2. Although frequency-dependent measurements were not made at all temperatures, we believe all shifts above about 65°K are true Knight shifts. Below this temperature, deviations from the Curie-Weiss hyperbola are seen in Fig. 2.

Positive K_0 values are traditionally observed and most easily rationalized. The negative K_0 seen here may be associated with the difference in diamagnetic effects in the metal and in the reference salt, but it may also have other origins. Negative K_0's are not unknown in the literature, although there is some tendency to overlook them when they appear. Negative K_0's are more usual at the less magnetic sites in intermetallic materials (such as Be in $CrBe_{12}$). This behavior may be connected with the magnetization distributions associated with such materials.

The Knight shift may also be plotted[6] against the susceptibility, χ, using the data for χ vs T from Ref. 2. Such a plot (not shown here) is a straight line with a $\chi=0$ intercept of $K_0=-(0.08\pm0.02)\%$. The slope of this line yields the paramagnetic effective field, H_{eff}^{para}. A least-squares determination of this quantity yields $H_{eff}^{para}=-3$ kG/μ_B per formula unit, at a Be site.

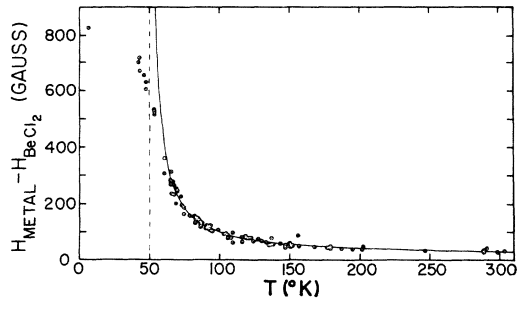

FIG. 2. Magnetic field shifts ($H_{metal}-H_{BeCl_2}$) for $CrBe_{12}$ at 8.000 MHz versus temperature. These shifts produce negative Knight shifts for temperatures above about 65°K, but are approximately independent of frequency at temperatures well below θ_p. The solid line represents a Curie-Weiss law with $\theta_p=50$°K.

Ferromagnetic results were obtained using a liquid-helium bath, and observing the resonance at different frequencies. The shift of the center of the resonance line is plotted as a function of frequency in Fig. 3 for a temperature of about 6°K. The broad line structure, shown in Fig. 1, is the origin of the large error bars placed here. The solid line plotted in Fig. 3 is H_{eff}^{para} multiplied by the experimentally observed magnetization per formula unit (determined at the magnetic field appropriate to the center of the resonance for each frequency). The shift of the line center in the ferromagnetic state, while not a traditional Knight shift, closely follows the magnetization. This indicates that the magnetization of $CrBe_{12}$ is a bulk effect, and not due to the presence of a second phase. This observation is valid whether or not impurities have driven the system ferromagnetic, as has been argued by Foner[7] for $ZrZn_2$. Also, the fact that H_{eff}^{para} supplies the scaling between magnetization and the resonance shift (i.e., $H_{eff}^{para}=H_{eff}^{ferro}$)[8] would seem to imply a ferromagnetic arrangement from Cr site to Cr site. Thus the local moment seems to equal the average bulk moment. If, for example, the Cr moments were arranged in a spiral, Fig. 3 would require the ferrimagnetic components of the spiral to cancel out at each Be site. This is possible, but unlikely.

The hyperfine field, seen in Fig. 3, permits some insight into the magnetization distribution within the unit cell in $CrBe_{12}$. In attempting this, we will assume that the hyperfine fields seen at a Be site arise predominantly from the conduction-electron spin moments residing at that site. We will further assume that the conduction-electron hyperfine field arises directly via the contact interaction (from s character) and/or from

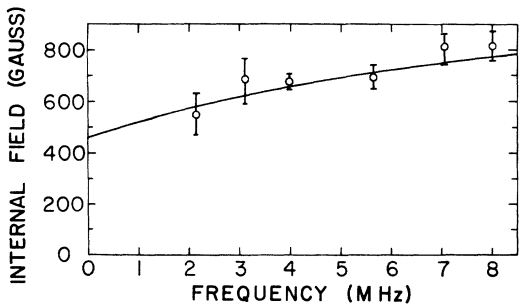

FIG. 3. Measured field shifts (relative to $BeCl_2$ solution) in ferromagnetic $CrBe_{12}$ at approximately 6°K. The solid line is the product of H_{eff}^{para} with the magnetization per formula unit obtained at 4.2°K.

core polarization and/or from dipolar fields due to an aspherical spin-density distribution on the Be site. Spin dipolar fields arising from moments at Cr sites can also be estimated. Assuming a Cr moment equal to the bulk moment (~0.2 $\times \mu_B$ at 8 MHz), dipolar fields are obtained which, of course, vary for the three types of Be sites. These display a spread in fields whose magnitude is less than one-third the observed shift. (The actual estimate depends on the magnetization direction.) We suspect that these dipolar fields may be an important mechanism contributing to the linewidth, but are less important to the line shift.

Since the electronic band structure and, more particularly, the Fermi-surface character are not known, we estimate the moment at the Be site from the different possible choices. If the conduction electron moment were of atomic $2s$ character, a moment of ~$0.002\mu_B$ at the Be site, antiparallel to the net magnetization, would account[9] for the observed hyperfine field. It may be argued that little $2s$ character is expected in the polarized conduction bands. If instead, the hyperfine field is attributed to atomic $2p$- and/or $3s$-like character, a moment of ~$0.04\mu_B$ would account[10] for the observed field. This moment would also be antiparallel to the net magnetization. This estimate neglects any spin dipolar fields associated with the $2p$ character. Their inclusion[10] would not substantially modify the result (i.e., by no more than $\pm 0.02\mu_B$). From these estimates one would conclude that the total moment residing at all 12 Be sites in the unit cell lies between $0.02\mu_B$ and $0.5\mu_B$ (and probably in excess of $0.1\mu_B$), antiparallel to the net ferromagnetic moment[11] of $0.2\mu_B$.

These estimates suggest that the magnetism in $CrBe_{12}$ is "itinerant," with significant magnetization density off the Cr sites, and on the Be matrix. Such a suggestion contrasts with one's first natural expectation of a magnetically inert array of Be atoms. Neutron-diffraction results (while admittedly difficult to obtain) would be most interesting to have for this magnetic system.

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[1]NMR in ferromagnetic materials, discovered by A. C. Gossard and A. M. Portis [Phys. Rev. Letters 3, 164 (1959)], is reviewed by A. M. Portis and R. H. Lindquist, in Magnetism, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1965), Vol. IIA. References to zero-field, swept-frequency spectrometers are given in this review.

[2]N. M. Wolcott and R. L. Falge, to be published.

[3]The paramagnetic "moment" appropriate to this ratio depends on the model used, but the conclusion in this case is unchanged. See P. Rhodes and E. P. Wohlfarth, Proc. Roy. Soc. (London), Ser A 273, 247 (1963). A comprehensive review of "itinerant ferromagnetism" has been presented by C. Herring, in Magnetism, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1966), Vol. IV.

[4]In an NMR study of ^{9}Be in MBe$_2$ (M = Ti, Cr, Mn, and Cu), H. Saji, T. Yamadaya, and M. Asanuma [J. Phys. Soc. Japan 21, 255 (1966)] obtained lines with structure similar to ours (but at least an order of magnitude narrower) and attributed the structure to first- and second-order quadrupole effects. Some of the structure we observe may be due to the three different types of Be sites, but we reserve judgment at this time. We concentrate on the line positions in this Letter.

[5]The indicated uncertainty in K_0 is a measure of the reproducibility. The temperature intercept is obtained with a higher precision than ±1°K; the uncertainty arises from the temperature calibration.

[6]A. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).

[7]S. Foner, E. J. McNiff, Jr., and V. Sadagopan, Phys. Rev. Letters 19, 1233 (1967).

[8]The equality of H_{eff}^{para} from a plot of K vs χ and H_{eff}^{para} from usual[1] zero-field ferromagnetic nuclear resonance has been observed for other ferromagnets, e.g., E. D. Jones and J. I. Budnick, J. Appl. Phys. 37, 1250 (1966), in $GdAl_2$.

[9]In obtaining this, we have employed an estimated Be $2s$ hyperfine field of 300 to 400 kG. The Hartree-Fock prediction for the direct $2s$ contact interaction plus experience from Li for the (lesser) polarization of the $1s^2$ core is used for this estimate. This, and any other of the hyperfine fields, is violently sensitive to the atomic configuration of the atom in the metal.

[10]While core polarization due to p, d, or f shells is gnerally negative, there is experimental evidence that it is positive for open $2p$ (and $3p$) shells. We have used the value obtained [L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., Phys. Rev. 116, 87 (1959)] for the ^4S $2p^3$ state of N. This should yield the correct sign and roughly the correct magnitude for Be. The $3s$ hyperfine field is also positive and is expected to be of this same magnitude. The dipolar fields of a single $2p$ electron (of specific m_l value) are of the same order of

magnitude, but these are expected to be at least somewhat quenched by the environment.

[11]An antiparallel moment on the 12 Be sites implies a corresponding increase in the moment attributed to the Cr. Cr dipolar fields could then become quantitatively important (but only to the extent that there exists a moment on the Be). This does not affect our qualitative conclusions.

RANDOM IMPURITIES AS THE CAUSE OF SMOOTH SPECIFIC HEATS NEAR THE CRITICAL TEMPERATURE

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We present a modification of the two-dimensional Ising model which incorporates random impurities. The specific heat of this model is infinitely differentiable even at the critical temperature where it possesses an essential singularity. We find this specific heat to be in perfect quantitative agreement with the smooth peak recently observed by van der Hoeven, Teaney, and Moruzzi for $T \gtrsim T_C$ in the specific heat of EuS.

Recently very precise measurements of specific heats near the Curie or Néel temperature T_C have been carried out by several investigators: van der Hoeven, Teaney, and Moruzzi on EuS,[1,2] Handler, Mapother, and Rayl on Ni,[3] Teaney, Moruzzi, and Argyl on $RbMnF_3$,[4] Keen, Landau, and Wolf on dysprosium aluminum garnet,[5] and Robinson and Friedberg on $MnBr_2$.[6] These experiments share the striking property that the measured specific heats are smooth functions of the temperature even at T_C. In this paper we explore the possibility of attributing these smooth specific heats to the presence in the sample of random impurities.

These recent experimental results are somewhat puzzling if they are contrasted with the usual theoretical treatments[7] and models of (anti)ferromagnetic phase transitions. These theories predict that at T_C the specific heat will have some sort of observable singularity that is expressible in the form

$$\text{const} \ln|T-T_c| \text{ or } \text{const}|T-T_c|^{\alpha}, \tag{1}$$

where α and the constants may be different for T above or below T_C. However, these treatments are all overidealizations of the true physical situation because they deal with completely pure materials. To study the effect of random impurities on the form (1) in a concrete fashion we have constructed a modification of the two-dimensional Ising model which includes random impurities. We find that the specific heat at T_C is an infinitely differentiable function for which the form (1) does not provide an adequate description.

The model we consider is the two-dimensional rectangular Ising model in which all horizontal interaction energies E_1 are fixed and all vertical interaction energies $E_2(j)$ betwen the j and $j+1$ row are the same. However, $E_2(j)$, $j = 0, 1, 2, \cdots$, are considered to be independent random variables. The calculation of the specific heat which is based on recent work of Furstenberg[8] is rather lengthy and is reported elsewhere.[9] The final result for a particular narrow distribution of bonds E_2 of width w is that, to leading order in w, near T_C the specific heat is given approximately by

$$c_1[R(\delta)+c_2-\ln w^2], \tag{2}$$

where

$$R(\delta)=\int_0^{\infty} d\varphi\left[\frac{\partial^2}{\partial\delta^2}\ln K_{\delta}(\varphi)-(\varphi+1)^{-1}\right], \tag{3}$$

$$\delta=-(1-T/T_c)w^{-2}, \tag{4}$$

c_1 and c_2 are known constants, and $K_\delta(\varphi)$ is the modified Bessel function of the third kind of order δ. It can be shown that the integral $R(\delta)$ of (3) has an essential singularity at $\delta = 0$. It has been computed numerically and is plotted in Fig. 1.

When δ becomes large, the specific heat (2) re-