EFFECTS OF IMPURITIES ON HIGHER ORDER PHASE TRANSITIONS*

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Measurements of the linear thermal expansion coefficient α of Gd crystals have shown that T_c as well as the temperature dependence of α is a function of the electron-impurity mean free path. These results have allowed us to infer the temperature dependence of the coherence length ξ.

The nature of higher order thermodynamic phase transitions has recently attracted much interest. The results of certain theoretical models and conjectures and precise experimental measurements suggest that the various thermodynamic and transport coefficients X_i are singular according to the simple expression $X_i = \epsilon^{\lambda_i}$, where $\epsilon = |T - T_c|/T_c$ and λ_i is an exponent characterizing the singularity.[1] The object of many investigations is to measure a set of λ_i for a particular system and to compare them with various theoretical models and scaling laws[2] or with other systems. Implicit in the theoretical models and in most experiments is the assumption that effects due to impurities are unimportant or can be ignored. In this paper we present evidence from measurements of the thermal expansion coefficient α near the ferromagnetic critical point T_c in Gd that impurities may determine the behavior of various thermodynamic and transport coefficients if one is sufficiently close to T_c. For Gd we find that a supercritical region can be defined for $\epsilon < \epsilon_i$ when the temperature-dependent coherence length ξ becomes comparable with the spin-fluctuation mean free path, l_s.

Although many investigators look for anomalies in the specific heat C_p, we have chosen to measure the thermal expansion coefficient α. Since both coefficients are second derivatives of the Gibbs free energy of equal rank, one would expect each to have the same type of singular behavior. This is certainly true if the thermodynamic surface in the neighborhood of the singular point can be described by a cylindrical surface as the Pippard relations[3] show. In our investigation a three-terminal capacitance cell was used to measure Δl along the c axis of Gd single crystals versus T as obtained from a Pt thermometer calibrated by the National Bureau of Standards. In this cell the capacitance between a capacitor plate affixed to one end of the crystal and a stationary plate was measured with a General Radio Model 1615-A capacitance bridge. The entire cell was immersed in a constant-temperature water bath with a vacuum space isolating the outer jacket from the sample chamber which contained low pressure helium exchange gas. Relative temperature changes of a millidegree could be determined by a thermometer attached directly to the crystals, while absolute temperatures were measured to ±0.02°K. Sufficient thermal stability was attained that capacitance changes of 1 part in 10^6 could be resolved.

Single crystals of Gd were prepared from metal sponge obtained from the Lunex Company by vacuum annealing and by vacuum distillation techniques.[4] The single crystals used gave sharp Laue x-ray patterns and were oriented to within $\frac{3}{4}$ deg of the c axis. Mass spectrographic analysis of the samples showed the principal impurities to be traces of the other rare earths with Ti also present. Traces of Ta were present only in the nondistilled samples. The inverse resistance ratio $\Gamma = \rho(4.2°K)/\rho(294°K)$ has been used as a measurement of the amount of impurity present in each sample.

In Fig. 1 we present measurements of $\alpha_\parallel$ ($\parallel$ to c axis) vs $\ln\epsilon$ for a sample with $\Gamma = 0.0097$ and $T_c = 292.50 \pm 0.02$°K. The transition temperature is defined by the minimum value of α which corresponds to a maximum in the specific heat. One sees for $\epsilon \gtrsim 1 \times 10^{-3}$ that α may be represented by $\alpha_\parallel \times 10^6$ °K $= A_\pm \log_{10}\epsilon + B_\pm$, where $A_+ = 20.5 \pm 1.5$,

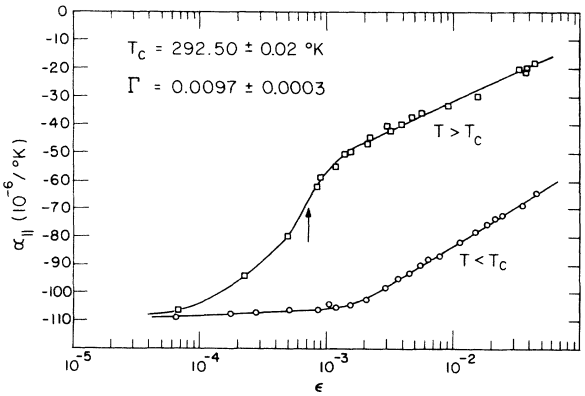

FIG. 1. $\alpha_\parallel$ vs ϵ for a sample with $\Gamma = 0.0097$.

$B_+ = 9.6 \pm 2.0$ for $T > T_C$, and $A_- = 27.0 \pm 2.0$, $B_- = -29.4 \pm 2.0$ for $T < T_C$. We note that the $T > T_C$ branch has an abrupt change in behavior at $\epsilon = 7 \times 10^{-4}$ and apparently has a different behavior for ϵ less than this value. Also there is a general bending of the $T < T_C$ branch at about the same ΔT.

A second sample was measured with $\Gamma = 0.026$ and $T_C = 291.4 \pm 0.1$°K. The sharp break in the $T > T_C$ branch occurred at $\epsilon = 3 \times 10^{-3}$. For this sample $A_+ = 18.0 \pm 2.0$, $B_+ = 20.4 \pm 3.0$ for $T > T_C$, and $A_- = 21.0 \pm 2.0$, $B_- = 2.8 \pm 3.0$ for $T < T_C$. From these two samples and data on two samples of larger Γ by Voronel et al.,[5] we have found a rather strong dependence of T_C on Γ which is indicated in Fig. 2.

Although this result, which we previously noted,[6] is important and can qualitatively be explained on the basis of a scattering factor $e^{-r/l}$ modulating the exchange interaction, we make no further note of this as we are interested in the behavior of $\alpha_{\|}$ with respect to Γ.

We now address ourselves to the abrupt break in the curves at T_i (defined as the inflection point) in the upper curve in Fig. 1. Using T_i from our samples and the two samples of Voronel we find a strong dependence of $(T_i - T_C)/T_C$ on Γ which is indicated in Fig. 3. These results may be fitted to a power law

$$[(T_i - T_C)/T_C]^{-\lambda} = A\Gamma^{-1}. \quad (1)$$

The exponent λ is found to have the value 0.72 ± 0.04.

We conjecture that the change in behavior occurring at T_i corresponds to the temperature at which the temperature-dependent correlation length $\xi(\epsilon)$ describing the fluctuation spectrum becomes comparable with the mean free path corresponding to processes which tend to destroy the order parameter. In this case one would expect the relevant mean free path to be that corresponding to spin-fluctuation scattering. Another way of seeing how a new behavior can arise is to say that ξ depends on l when $\xi \sim l$ and thus the fluctuation spectrum is changed.[7] The functional form of $\xi(\epsilon, l)$ in this supercritical region when $\xi \sim l$ is as yet unknown. The coherence length near T_C is frequently believed to diverge according to $\xi = \xi_0 \epsilon^{-\nu}$. Noting that Γ is inversely proportional to the electron-impurity mean free path $l_{ei} \approx$ spin fluctuation mean free path l_S, one may set $\lambda = \nu$ if T_i is the temperature at which $\xi \approx l_S$. The value obtained for ν is then 0.72 ± 0.04. This is in good agreement with the neutron measurements of ξ on other magnetic systems.[1] By estimating the product $\Gamma l_{ei} = m v_F / \rho_{294°K} n e^2$ using the free electron model one can also obtain a rough value of ξ_0. This estimate gives $\xi_0 = 2.6$ Å, which is less than the nearest-neighbor spacing in Gd. Because of the extremely high neutron absorption cross section in Gd there have been no neutron scattering measurements of ξ for Gd.

We now inquire about what evidence there is for impurity effects in other systems. We will only note some instances in the data for Ni and Fe, but other examples can be found.

Recent measurements of the temperature coefficient of resistivity of Ni show an abrupt change in behavior for $T > T_C$ at $\epsilon = 5 \times 10^{-3}$.[8] In this case as with our measurements of $\alpha_{\|}$, for $T > T_C$ the strength of the divergence increases for a short range of ϵ before the coefficient assumes a finite value at T_C. The specific-heat data of Ni

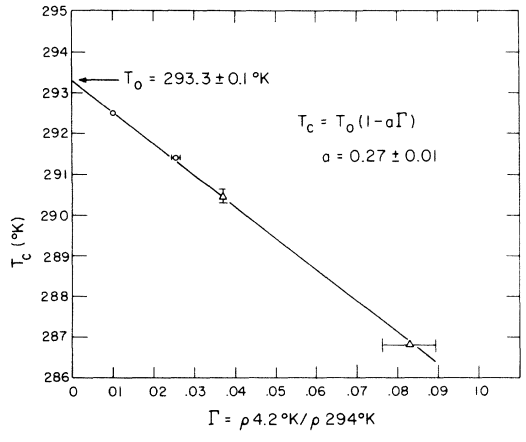

FIG. 2. T_C vs Γ. Circles: this investigation; triangles: Voronel et al., Ref. 5.

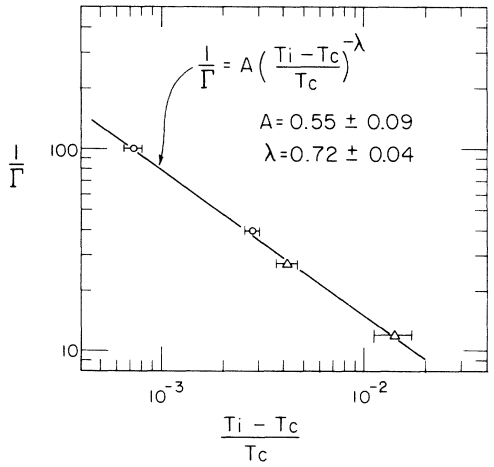

FIG. 3. Log-log plot of $1/\Gamma$ vs $(T_i - T_C)/T_C$. Circles: this investigation; triangles: Voronel et al., Ref. 5.

films[9] for $T > T_C$ also show an anomaly at $\epsilon = 2 \times 10^{-2}$ with almost all the data being taken for smaller ϵ. In addition it has been reported[10] that for Ni the exponent β characterizing the spontaneous magnetization changes from $\frac{1}{3}$ to $\frac{1}{2}$ at $\epsilon \approx 6 \times 10^{-3}$. We find that these observations are consistent with calculations of $(T_i - T_C)/T_C$ based on estimated or given impurity levels for these samples.

The spin correlation range in Fe deduced from neutron scattering[11] when plotted against $\ln\epsilon$ shows a deviation from $\nu \approx \frac{2}{3}$ behavior for $\epsilon < 6 \times 10^{-3}$. Again this change in behavior occurs at a value of ϵ consistent with the value inferred from the relation $\xi(\Delta T) \approx l_{ei}$. Also this is evidence that for $T - T_C < T_i - T_C$ the coherence length may depend on the mean free path.

In conclusion we have in this paper shown that the value of T_C as well as the detailed behavior of thermodynamic coefficients near a higher order phase transition as the supercritical region is entered may be strongly determined by impurity concentrations. By observing the values of ϵ for which $\xi \approx l_{ei}$ we have been able to infer the temperature dependence of the range of spin fluctuations in Gd.

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DIRECT OBSERVATION OF COHERENT EXCHANGE SCATTERING BY LOW-ENERGY ELECTRON DIFFRACTION FROM ANTIFERROMAGNETIC NiO

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Coherent exchange scattering has been observed in low-energy electron diffraction from antiferromagnetic NiO. Half-order diffraction beams which correspond to the translational symmetry of the magnetic cell occur below the Néel temperature, $T_N = 525°K$, and disappear at T_N. These beams are attributed entirely to exchange scattering because of their intensity, which is much too great to be accounted for by direct dipole-dipole and spin-orbit interactions.

This paper reports on the first experiment in which coherent scattering from an ordered magnetic spin system has been observed by electron diffraction. Not only does low-energy electron diffraction (LEED) from antiferromagnetic crystals provide an additional method for probing magnetic structure, but, perhaps more importantly, it is the most direct means now available for studying the role of exchange in electron scattering.

Spin ordering in antiferromagnetic NiO leads to a magnetic cell having dimensions twice that of the chemical cell. The arrangement of spins, as determined by neutron diffraction,[1] is represented in Fig. 1(a). If this spin configuration is not altered at the surface, the translational sym-