Specific heat and resistivity of an amorphous alloy, $Fe_{34}Pd_{46}P_{20}$, near its ferromagnetic phase transition

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Specific-heat and resistivity measurements are reported for an amorphous ferromagnetic alloy $Fe_{34}Pd_{46}P_{20}$. We find a sharp, well-defined phase transition into the ferromagnetic state at 205 K, despite the low concentration of magnetic iron atoms. Analysis of the temperature derivative of the resistivity yields information on the critical exponents $\alpha = \alpha' = -0.065 \pm 0.05$. The specific heat shows only a small anomaly at the ferromagnetic transition. This behavior is explained by the alloy's proximity to the percolation threshold for a uniform ferromagnetic state.

I. INTRODUCTION

Although there have been a considerable number of investigations of the behavior of phase transitions in pure well-ordered magnetic materials,[1,2] the behavior of disordered systems, those which have been diluted by impurities, broken bonds, or other nonmagnetic elements, has only recently undergone serious experimental and theoretical investigation. Questions about these materials which have generated the most interest are those that probe the validity of universality theories and scaling relations between critical exponents, and those that probe the effects of increasing disorder and dilution on the phase transition. Theoretical investigation of these questions has progressed a great deal with the introduction of renormalization-group techniques. These calculations of the behavior of quenched random systems have indicated that there should be a well-defined, sharp phase transition with asymptotically universal values of the critical exponents.

The formal arguments by Harris and Lubensky[3] are a development of earlier ideas of Harris.[4] He pointed out that when the specific-heat exponent α is less than zero, scaling relations between the critical exponents would indicate that the coherence length and the correlated volume would be diverging faster than fluctuations of the transition temperature caused by inhomogeneous local concentrations of magnetic ions. For temperatures close to T_C, the system would look homogeneous on the scale of the coherence length and the transition will be sharp.

More recently, predictions have also been made about the behavior of these random systems when the magnetic concentration has been diluted sufficiently so that the disordered system is close to its percolation threshold. Ising-model calculations made by Reidel, Jayaprakash, and Wortis[5] indicate that as the concentration of magnetic ions is decreased, the width of the critical region and the size of the specific-heat anomaly at the phase transition is also decreased.

Experimentally, there has been much less progress. Although there have been some experiments performed using alloys of elemental magnets with noble metals,[6,7] the results of these experiments are clouded by the possibility that the impurities form large-scale clusters and the alloy systems are not truly random. More recently, two different experimental approaches have been used with better success. One approach has been to study insulating random antiferromagnetic systems using a mixed binary-transition-metal fluoride perovskite, $RbMn_{0.05}Ni_{0.5}F_1$.[8] The other approach takes advantage of the discovery that rapidly quenched metallic glasses can become ferromagnetic.[9] These quenched metallic systems can be made with a high concentration of magnetic atoms, such as $Fe_{75}P_{15}C_{10}$ or $Co_{70}B_{20}P_{10}$, or with low concentrations of magnetic atoms, $Fe_xPd_{80-x}P_{20}$ ($13 \leq x \leq 44$).[10] The more concentrated systems have magnetic-ion densities which are far above the percolation threshold, and the results on these systems have given a great deal of support to the idea that a random system can display a sharp phase transition. Magnetic studies on amorphous $Co_{70}B_{20}P_{10}$ indicate that the critical indices for the magnetization, susceptibility, and field dependence of the magnetization are well defined and have asymptotic limits for $T \rightarrow T_C$ which are consistent with scaling relationships and predictions of universality.[11] Preliminary studies of the specific heat[12] of this material also indicate a sharp, cusped anomaly. In amor-

phous $Fe_{75}P_{15}C_{10}$ the specific heat has also been measured.[13] Analysis of the anomaly at T_C indicates that it has a cusped behavior rather than a divergent behavior, i.e., the critical index $\alpha = \alpha' < 0$. When $Fe_{75}P_{15}C_{10}$ is annealed above its glass-forming temperature, the material forms clusters of varying stoichiometric composition and the specific-heat anomaly disappears completely.

The experiments on the concentrated alloy systems have been very significant and provide some indication that the renormalization-group calculations are based on a reasonable model of the real physical system. We have chosen, however, to test the limits of the validity of the theory of phase transitions in random systems. We present experimental evidence that there is a well-defined phase transition in amorphous ferromagnet $Fe_{34}Pd_{46}P_{20}$, which is very dilute compared to the $Fe_{75}P_{15}C_{10}$ and $Co_{70}B_{20}P_{10}$ systems.

A detailed study[14] of the magnetic properties of the amorphous alloy system $Fe_xPd_{80-x}P_{20}$ for the concentrations $13 \leq x \leq 44$ have been made. The Mössbauer effect was used to determine the hyperfine-field distribution as a function of composition and temperature, and also complementary magnetization measurements were used to determine the transition temperature associated with the magnetic phase. A plot of the magnetic-transition temperature as a function of concentration reveals a sharp change in slope at $x \simeq 26$. For higher concentrations there is a long-range magnetic order and a net magnetization of the sample below T_C; for lower concentrations the magnetic order is much more localized. At these low concentrations there is no net magnetization and the samples appear to be in a spin-glass state. The samples that we have chosen for this study ($Fe_{34}Pd_{46}P_{20}$) are above the percolation threshold for ferromagnetism but still have less than half the concentration of the $Fe_{75}P_{15}C_{10}$ alloy.

In this paper we present detailed measurements of the specific heat and the resistivity of samples of $Fe_{34}Pd_{15}P_{20}$ near the ferromagnetic phase transition. The temperature derivative of the resistivity near the phase transition indicates that the phase transition is sharp and has a cusped behavior. The specific-heat measurements on the same material show only a very weak anomaly, however. Both of these experiments provide valuable clues as to what is happening at the ferromagnetic phase transition in a random and severely diluted system.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

The amorphous state of the $Fe_{34}Pd_{46}P_{20}$ alloy which we studied in this investigation was achieved by rapid quenching from the melt at a cooling rate of $\sim 10^6$ K/sec using the "piston and anvil" technique.[15] Details of this alloy's preparation have been previously published.[16] The x-ray and electron-diffraction patterns for the liquid-quenched samples showed only diffuse halos which are characteristic of a liquid structure. Analysis of the x-ray diffraction pattern suggests that the structure of amorphous alloys of this type can be approximated by a model with a dense random packing of hard spheres (the transition metals, Fe and Pd) with a glass former (such as P) occupying the Bernal holes present in this model.[10,16] It has been found that the Fe and Pd atoms appear to substitute freely in this structure, and the short-range order resembles that of crystalline Fe_3P and Pd_3P.[10,16]

Specific-heat measurements have been made on samples of amorphous $Fe_{34}Pd_{46}P_{20}$ using two techniques of small-sample calorimetry, an ac technique using chopped light as a heat source, and a scanning calorimetry. The former method[17] has been used very successfully for small metallic samples, exhibits a high relative accuracy, and is particularly well suited for measurements near phase transitions since the data are taken continuously while the temperature is slowly increased or decreased. In the ac calorimeter, both the sample's average dc temperature and the ac temperature oscillations which are induced by the heat pulse are measured with a double cromel-alumel thermocouple junction. The absolute temperature is determined with reference to an ice-water bath. The heat leak between the sample and the copper reference block in the calorimeter is provided by introduction of a helium exchange gas. Although the ac technique gives very high relative accuracy, absolute calibration is dificult without a detailed knowledge of the heat absorbed from the external light source. To check the absolute scale of the specific heat and the overall temperature dependence of our results, scanning calorimetry was performed with a Perkin-Elmer Differential Scanning Calorimeter model II(DSC).

These specific heat results on $Fe_{34}Pd_{46}P_{20}$ are shown in Figs. 1 and 2. Figure 1 shows the temperature

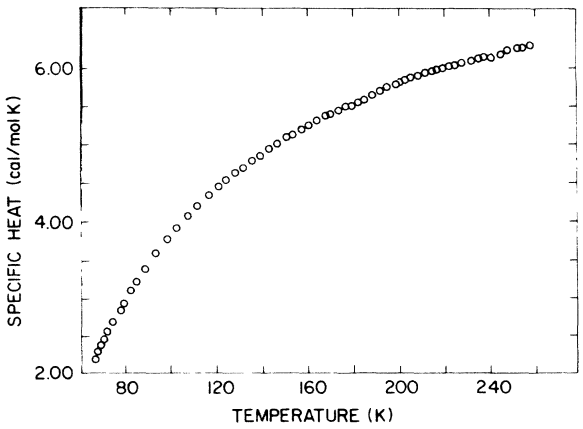

FIG. 1. Specific heat of $Fe_{34}Pd_{46}P_{20}$ as a function of temperature.

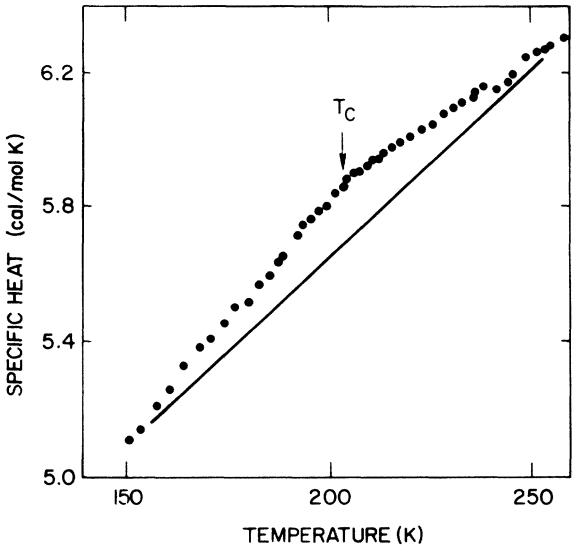

FIG. 2. Details of the specific heat near the ferromagnetic transition T_C at 205 K. The straight line provides a visual comparison to emphasize the deviations at T_C.

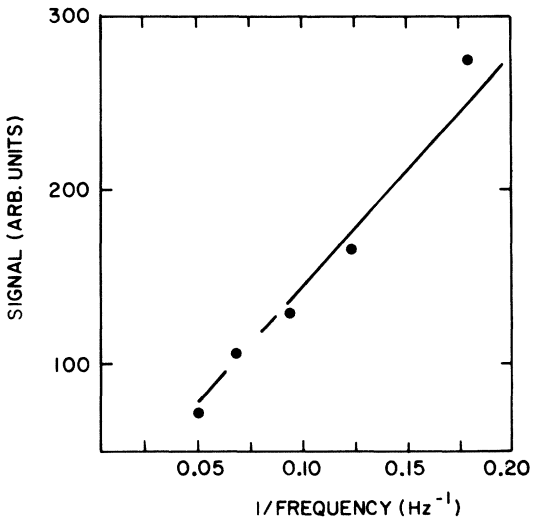

FIG. 3. Magnitude of thermocouple voltage oscillations as a function of period of the oscillations. Linear relationship implies $\Delta T \propto C_p^{-1}$.

dependence of the specific heat from 50–300 K. Although it is not very visible in this figure, there is a small, broad anomaly in the specific heat which has its maximum deviation from a smooth-lattice-background contribution at 205 K. We show more detailed specific-heat data for temperatures close to 205 K in Fig. 2. The straight line provides a visual comparison to emphasize the small specific-heat anomaly which is associated with the sample's transition into the ferromagnetic state. These data were taken using a light chopping, and hence heat pulsing, frequency of 13.5 Hz. We have taken additional data at 5 and at 22 Hz. There is complete agreement between these three data sets, to within our limits of accuracy, and all three frequencies lie within the correct operating range of the ac technique.[17] This operating range is determined by the requirement that the internal relaxation time of the sample and the sample's thermocouple junction be short when compared to the period of the heat pulse, and that the period of this heat pulse should also be short when compared to the thermal relaxation time of the sample to the copper heat sink. When these conditions are met, the amplitude of the temperature oscillations of the sample (at a fixed heat sink temperature) are inversely proportional to the frequency of the chopped heat pulse. Figure 3 shows this linear relationship for one of the $Fe_{34}Pd_{46}P_{20}$ samples which we measured.

The systematic noise associated with this specific-heat measurement increases with decreasing frequency while the amplitude of the signal decreases with increasing frequency. Our measured signal to noise ratio was best at 13.5 Hz. The relative accuracy of our measurements at this frequency is 0.25% of the measured heat capacity at 205 K, but is possibly as high as 0.5% of the total specific heat when we used 5 or 22 Hz. Although the data were continuously recorded as a function of temperature, and the relative precision of our temperature measurement was high, the digitization of our data introduced error into our temperature of 0.1 K, which corresponds to a reduced temperature $t \equiv |(T - T_C)/T_C| = 5 \times 10^{-3}$.

Since we failed to see a large anomaly in the specific heat associated with the transition of $Fe_{34}Pd_{46}P_{20}$ into a ferromagnetic state, we wanted to determine if our results were sample dependent. We found no variation of our results among at least five different samples that we measured.

In addition to the specific-heat results, we have made precision measurements of the resistivity of this amorphous ferromagnet. We use these resistivity measurements to give us more information about the phase transition between the nonmagnetic and magnetic state. There have been several theoretical papers which have calculated the temperature dependence of the resistivity in the vicinity of the ferromagnetic phase transition.[18,19] These calculations indicate that the temperature derivative of the resistivity should have an anomaly at T_C, and that the critical temperature dependence of this anomaly should be the same as the specific heat, $\partial\rho/\partial T \propto t^{-\alpha}$. The resistivity of a magnetic metal has a component which originates in spin-flip scattering in addition to the dominant contributions from impurity and phonon scattering. Near the transition into the ferromagnetic state, the spin-flip scattering of the electrons is enhanced by spin

fluctuations which can be described by the spin-spin correlation function. The spin-spin correlations are a function of both temperature and wave vector in reciprocal space. The static, $k=0$ mode of this correlation function diverges at the ferromagnetic transition temperature T_C, but the correlation function at larger wave vector does not diverge according to model calculations.[20] Since the resistivity is dominated by electrons which scatter through large angle, the large-momentum spin fluctuations with wave vector k near $2k_F$ influence the resistivity more than the more divergent $k=0$ or small-k fluctuations. The temperature derivative of the correlation function for large k is responsible for the cusped anomaly in the resistivity derivative.[18] Measurements of the resistivity on the ferromagnetic elements nickel[21] and iron[22] have demonstrated the validity of this theory.

The resistivity measurements were made using a standard four-probe dc technique. Current was passed in both directions in the sample, and the average voltage measurements were used. This precaution, along with careful mounting of the sample on an isothermal block, eliminated the possibility of spurious results due to temperature-dependent thermoelectric effects. Temperature measurement was made with a copper-constantan thermocouple while the sample temperature was allowed to drift at a rate of 10 K/hr.

Although there is very little change in the absolute value of the resistivity from 180 to 230 K, the extreme precision possible in resistivity measurements allows a smooth temperature derivative to be taken. Both the resistivity and the temperature derivative of the resistivity are shown in Fig. 4. The temperature derivative was taken analytically by minimizing the square of the difference between 11 data points and a quadratic function, finding the slope of this fitted function at the midpoint, then sliding the averaging group by one datum point. Since there is a better-defined anomaly in the temperature derivative of the resistivity than in the specific heat, we have analyzed the critical-temperature dependence of this derivative in greater detail.

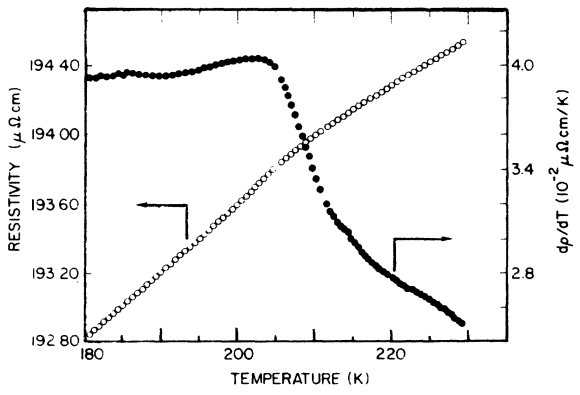

FIG. 4. Resistivity and temperature derivative of the resistivity as a function of temperature. The derivative was taken numerically by fitting to groups of 11 data points.

In Fig. 5 we have plotted the temperature derivative of the resistivity as a function of the log of the reduced temperature for temperatures which are above and below $T_C=205$ K. The data are the same as the 11-point derivative, as shown in Fig. 4. In order to determine the asymptotic value of the critical exponent α, we fit these results to

$$\frac{\partial\rho}{\partial t}=\frac{A}{\alpha}(t^{-\alpha}-1)+B \ ,$$

using a routine which minimizes the square of the deviations from this function as a function of the parameters A, B, and α. The transition temperature T_C was chosen to minimize the region above and below T_C where there was large systematic deviation from the above function. The systematic deviation was less than the random deviation of our data from this fitting function in the temperature region $1.0>|t|>0.01$. We find

$$\alpha(T>T_C)=\alpha'(T<T_C)=-0.06\pm0.05$$

for the plotted 11-point derivative, $\alpha=\alpha'=-0.1\pm0.1$ for a three-point derivative. There is systematic deviation of the data for $|t|<0.01$ which is similar to the rounding seen in crystaline solid measurements.[2,21,22] The value of α that we measure is consistent with the predictions of universality for a three-dimensional Heisenberg model,[1,23] but we do not find $A^+(T>T_C)/A^-(T<T_C)=1.0$, which is what the ratio of the coefficients is expected to be for the specific heat above and below T_C.[23] Although there is a prediction that the temperature dependence of the resis-

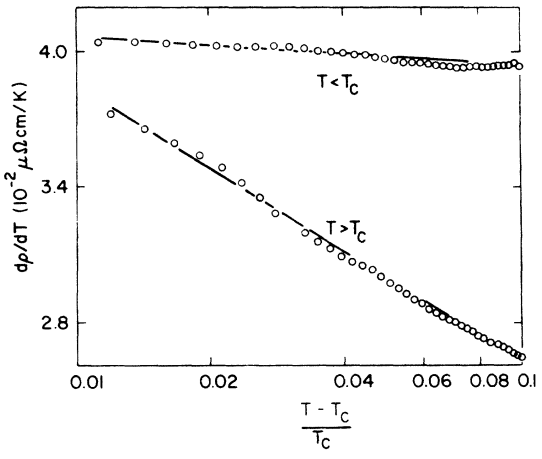

FIG. 5. Plot of the resistivity derivative as a function of the log of the reduced temperature $t\equiv|(T-T_C)/T_C|$. The lines through the data are a least-squares fit for $\alpha=\alpha'=-0.06\pm0.05$.

tivity should be the same as that of the specific heat, there is no prediction about the amplitude of this prefactor on either side of T_C.

III. DISCUSSION

There are several experimental details of the specific heat and resistivity results which must be examined in order to make a clear comparison of our data with theoretical expectations for a dilute-random, quenched-magnetic material. First of all, there is no large specific-heat anomaly associated with the phase transition between the paramagentic and ferromagnetic states. We see a broad anomaly with a small deviation at T_C from a smooth-lattice background. Second, the total change in the resistivity is small near the phase transition, but the temperature derivative of this resistivity does show some evidence of critical behavior. For reduced temperatures $|t| \leq 0.01$, we do see asymetric rounding of the derivative, but this rounding may be due to experimental limitations of our resolution.

The demonstrated existence of a well-defined phase transition even in this dilute amorphous alloy $Fe_{34}Pd_{46}P_{20}$, and the agreement of the critical exponents α and α' with the predictions of universality theory give further support for the claims of the renormalization-group calculations. Random impurities or broken bonds and dilution do not prevent a sharp phase transition.[3,4] A comparison of our resistivity results with resistivity measurements on NiCu alloys[7] points out that the randomness and quenched nature of the samples is important, however. In the nickel alloys the resistivity anomaly has been completely suppressed by the time the nickel concentration has been reduced to 40%. This is a direct result of the formation of clusters that are not present in our quenched amorphous system.

It is possible to understand qualitatively the small specific heat anomaly at the ferromagnetic phase transition and the apparent lack of enthalpy associated with this change of state. Previous work clearly indicates the proximity of this alloy $Fe_{34}Pd_{46}P_{20}$ to the percolation threshold at 26% iron concentration. It also shows the large sensitivity of the transition temperature to the concentration of iron slightly above this percolation threshold; $T_C = 80$ K for 26% iron, $T_C = 319$ K for 44% iron.

A magnetic system which is diluted to the percolation threshold[24] consists of clusters of magnetic atoms with multiple connected bonds to other magnetic atoms, but the clusters are connected together by magnetic-bond chains that are more filamentary in character. The connectivity of the ferromagnetic state, therefore, is not truly three dimensional, and the ferromagnetic phase transition that we see at 205 K has some lower-dimensional character.[25] The fluctuations which are dominant near these lower-dimensional phase transitions are low-wave-vector long-range fluctuations which do not contribute strongly to the enthalpy. The large-wave-vector short-range fluctuations which normally contribute the bulk of the enthalpy to the phase transition in a concentrated magnetic system are severely damped at this phase transition because they are dominated by the exchange interaction between pairs of atoms that are in fact nearest neighbors.

The magnitude of this nearest-neighbor exchange interaction energy can be estimated for our sample. This exchange energy is larger than the transition temperature for the $Fe_{44}Pd_{36}P_{20}$ alloy (319 K),[14] and lower than the exchange energy for pure crystalline iron (104K).[2] Probably the best estimate of this interaction energy is the ferromagnetic transition temperature of the amorphous binary alloy $Fe_{80}P_{20}$. Logan and Sun[26] find this transition temperature to be 560 K. All of these estimates are considerably larger than the 205 K transition temperature that we find. The three-dimensional transition within the cluster, then, is at a much higher temperature, and the majority of the large-energy short-range fluctuations should be frozen out by 205 K.

Although these large-wave-vector fluctuations are severely damped, they are not entirely absent since there are exactly the same number of spin fluctuations responsible for the anomaly that is seen in the resistivity. An interesting study might be made in the future by comparing the strength of the specific-heat anomaly with the resistivity anomaly across a series of successively diluted alloys of the same ternary series. Since both the specific heat and the resistivity are quantities which are related to an integration over the spectral distribution of the fluctuations, however, it is not possible to get direct information about the distribution of fluctuations between high and low wave vector.

The calculations by Reidel *et al.*[5] on the Ising models with random-bond defects was not extended to as low a concentration of magnetic bonds as are present in our experimental alloy, but certainly some comparison of our results with their predictions is fruitful. Their calculations predict that the large specific-heat anomaly which is seen in the more concentrated alloys should diminish both in amplitude and in the width of the critical region as the number of broken bonds increases. This is in qualitative agreement with what we see. It is not completely clear, however, that the width of our critical behavior is as vanishingly small as they would expect for such a dilute system. We find reasonable power-law behavior out to reduced temperatures at least as large as $|t| = 0.5$.

A recent mean-field theory on spin-glasses based on a cluster model suggests that the specific heat of these magnetic systems as a function of temperature should

exhibit only a rounded maximum and a very small cusp at the phase transition temperature.[27] It is possible that these theoretical results are useful in explaining our experimental findings for amorphous $Fe_{34}Pd_{46}P_{20}$, which is very close to the spin-glass composition range.

In summary, then, we find that there is a well-defined phase transition in a dilute amorphous ferromagnet $Fe_{34}Pd_{46}P_{20}$. Resistivity measurements indicate that the phase transition is sharp and has a critical exponent $\alpha = \alpha' = -0.06 \pm 0.05$. Although the specific-heat measurements indicate that there is little enthalpy change at the ferromagnetic transition at 205 K, this can be understood since the alloy is very close to the percolation threshold.

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