Magnetic Behavior of CuMn Dilute Alloys

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The electron-spin resonance of CuMn dilute alloys was observed for samples annealed in an ultra-high-vacuum system. An anomaly in the ESR linewidth for 4.3 and 2.0 at.% Mn alloys was observed in the temperature region where Kouvel observed an anomaly in the resistivity. This anomaly should be considered as an effect of magnetic short-range order among the diluted Mn atoms. The antiferromagnetic phase transition temperature T_N was estimated from the temperature variation of the resonance position. The T_N was about 60 and 20°K for the 4.3 and 2.0 at.% Mn alloys, respectively.

1. INTRODUCTION

THE magnetic behavior of CuMn dilute alloys which contain Mn atoms distributed at random in solid solution has been studied by many researchers. The pioneer work on the electron-spin resonance (ESR) and the susceptibility of CuMn dilute alloys has been done by Owen *et al.*[1] According to the susceptibility measurements, the alloys have shown an antiferromagnetic behavior at low temperature. But the fact that the Weiss temperature is positive is very interesting. Kouvel[2] has pointed out the possibility that CuMn dilute alloys are in a mixed ferromagnetic-antiferromagnetic state at low temperature, and from the electrical resistivity of the alloys he has estimated the antiferromagnetic ordering temperature, although the onset of the magnetic order is usually spread over an appreciable temperature range. But the antiferromagnetic ordering temperature estimated by Kouvel is much too high compared with the temperature indicated by Griffiths[3] from (ESR) data. According to Kouvel's estimate, the Néel temperature was about 150°K for a 5.5 at.% Mn alloy, but in this temperature region no anomalies could be found in the ESR. Griffiths estimated the antiferromagnetic ordering temperature from the temperature dependence of the critical field H_c for 4 and 15 at.% Mn alloys, which were 43 and 115°K, respectively.[3]

The remarkable feature of the present experimental results is observation of an anomaly in the linewidth of the ESR in the temperature region which agrees with that estimated by Kouvel from the electrical resistivity. This anomaly seems to be associated with short-range order in the alloys. On the other hand, the resonance-point-versus-temperature curve shows a steep rise at a rather lower temperature than that of Kouvel. From these results, the present authors conclude that the onset of long-range antiferromagnetic order should be determined from the steep rise of the curve of resonance point versus temperature. The present results for the ESR are different from the earlier works[1,3] in the temperature dependence of the linewidth. The discrepancy between the results of the other researchers and ours is due to the effects of oxygen absorbed in alloys,[4] as explained in a later section.

2. SAMPLES

A. Bulk Samples

Copper metal was supplied from the Furukawa Central Research Laboratory with a nominal purity of 99.999% and manganese metal was obtained from the Johnson Matthey Co. with a nominal purity of 99.999%. Alloys were made by melting the two components under an atmosphere of argon in an arc furnace. The specimens were annealed in an ultra-high-vacuum system of 10^{-8}–10^{-9} Torr at 300°C for 24 h and at about 850°C for 48–120 h. The specimen used in the ESR experiments was rod-shaped, about 10 mm long by 1 mm in diameter, and sealed in a vacuum quartz tube to avoid the contamination of sample surfaces. We must be especially careful not to absorb oxygen in the alloys in the course of sample preparation. The effect of oxygen on the alloys is shown in Fig. 1 for the 4.3 at.% Mn-Cu alloy. Circles, triangles, and crosses in this figure show the measured values for the specimens denoted (a)–(c) when they were annealed at 850°C in a vacuum of $\sim 10^{-3}$, 1×10^{-6}, and 3×10^{-8} Torr, respectively. When specimen (c) is exposed to the air for a moment, the linewidth at room temperature becomes broader by about 70 Oe than the initial value of 140 Oe as shown by the double circle in this figure. These results suggest that the magnetic behavior of these alloys is very sensitive to oxygen in the atmosphere. Mn concentration was determined by x-ray analysis of the lattice parameter.[5]

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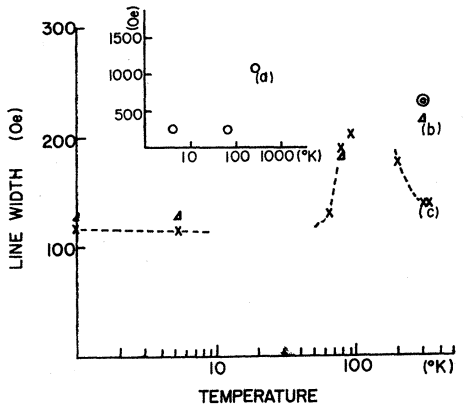

FIG. 1. Temperature dependence of the linewidth; circles, triangles, and crosses show the linewidth for the 4.3 at.% Mn–Cu alloy annealed at $\sim 10^{-3}$, 1×10^{-6}, and 3×10^{-8} Torr, respectively.

B. Powder Sample

Powder samples were prepared by diffusion of Mn impurities in Cu particles. These particles mixed with alumina powder were heated at 300°C for two days under an atmosphere of hydrogen and then heated to 900°C for about three days in an ultra-high-vacuum system ($\lesssim 10^{-8}$ Torr). The alloys were sealed in a vacuum quartz tube in order not to be exposed to air. The maximum particle sizes used in this experiment are about 2000 Å in diameter. These particle diameters are the same order as the skin depth.

3. ELECTRON-SPIN RESONANCE

ESR was observed in the temperature region from 300 down to 1.2°K for CuMn dilute alloys. The resonance position and the linewidth were measured by a conventional 24-GHz superheterodyne spectrometer.

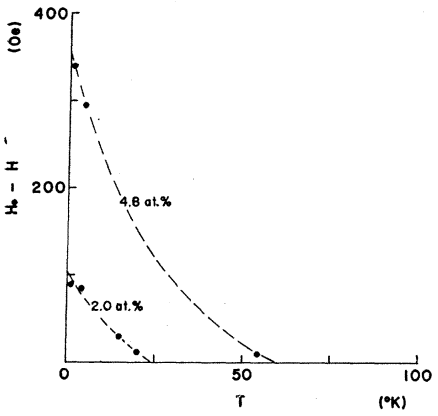

FIG. 2. Temperature variation of the shift at resonant frequency of 24 GHz. H and H_0 show the resonance fields for CuMn dilute alloys and DPPH, respectively.

A. Resonance Position

The line shape is symmetrical and independent of temperature in the powder sample. In this sample for the 1.2 at.% Mn alloy, the g value is estimated to be 2.004 at room temperature and 2.008 at 90°K. For the rod-shaped alloys containing 4.3 and 2.0 at.% Mn, the resonance position shifts to lower fields with decreasing temperature below about 60 and 20°K, as given in Fig. 2. The correction for the demagnetizing field in the bulk sample was made in the present data. H and H_0 show the resonance fields of the alloys and diphenylpicrylhydrazyl (DPPH), respectively.

B. Linewidth

Figure 3 shows the experimental result for the linewidth versus temperature in the cases of a few Mn

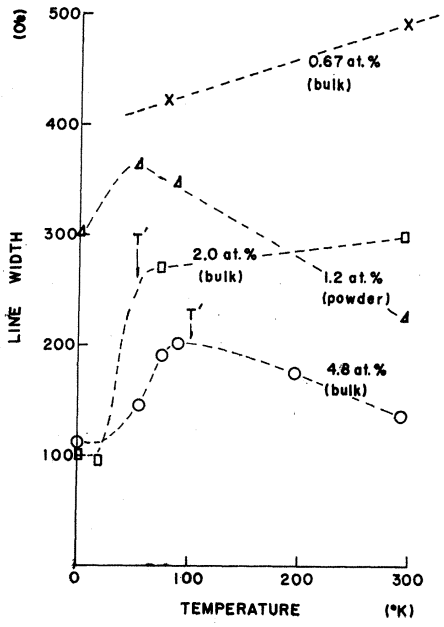

FIG. 3. Temperature dependence of the ESR linewidth.

concentrations. The temperature dependence is quite different from that of the earlier workers.[1,3] The present result for the 4.3 at.% Mn alloy shows the fact that the linewidth increases with decreasing temperature in the high-temperature region and decreases very steeply at lower temperatures, as shown in Fig. 3. This anomalous change in the linewidth seems to disappear with decreasing concentration of Mn impurities in the alloys. The line shape also varies with temperature for the bulk sample in the high-temperature region. The peak-to-peak width for the first derivative may be affected by the line shape, but such an effect is considered to be negligible in the present experiment. This is inferred from a similar behavior of the powder sample. The ESR signal from powder sample shows a

behavior equivalent to a higher Mn concentration alloy than that determined by x-ray analysis in the present case, as seen in Fig. 3, since Mn impurities in powder sample do not diffuse so uniformly as in the bulk sample. The linewidth for the powder sample is rather broad at low temperatures compared with the bulk sample. Perhaps this may be due to spurious line broadening from the mixed alumina powder. Griffiths[3] has observed an anomaly in the temperature dependence of the linewidth for the alloys cooled in a magnetic field down to a lower temperature than that of the onset of antiferromagnetic order. In the present experiment, the anomaly was observed at temperatures where the alloys are paramagnetic. Moreover, these alloys were cooled in zero magnetic field. The electrical resistivity was also measured for the alloys with 4.3 and 2.0 at.% Mn, for which an anomalous change was observed below 100 and 35°K, respectively.

4. DISCUSSION

The theoretical treatment of the magnetic properties of magnetically dilute systems is very difficult. Sato *et al.*[6] and Klein *et al.*[7] have studied the magnetic behavior in dilute solutions. They discussed the magnetic properties on the basis of an Ising model for a simple ferromagnet and antiferromagnet.

Their approximations seem not to apply for CuMn alloys with rather high Mn atoms ($\gtrsim$1 at.% Mn), because the alloys show certain unusual magnetic properties observed by Kouvel[2] and by Griffiths[3] in the magnetic hysteresis loops and in the shift of the magnetic resonance position, respectively, when the alloys are cooled to very low temperatures in a magnetic field. Kouvel[8] has discussed the magnetic properties for CuMn alloys by the model in which the magnetic unit is a small ensemble of mutually interacting ferromagnetic and antiferromagnetic domains. The complex magnetic structure discussed by Kouvel seems to explain the magnetic behavior fairly well.

The present experimental results are qualitatively explained by the model. The anomaly in the ESR linewidth was observed as shown in Fig. 1 at about 100°K for 4.3 at.% Mn alloy. This temperature is close to the anomaly in an electrical resistivity observed by Kouvel. We suppose that the anomaly is due to short-range order in antiferromagnetic domains. The antiferromagnetic domain boundaries are considered to exhibit time-dependent fluctuation down to about 60°K for 4.3 at.% Mn alloy. The ESR at low temperatures is reasonably explained by the equation[1]

$$H=H_0^2-H_c^2, \quad H_c=(2H_EH')^{1/2}, \tag{1}$$

where H_0 is the resonance field for CuMn alloys at the paramagnetic state, H_c is the critical field, H_E is the average exchange field, and H' is the average anisotropy field. That is, from the frequency dependence of the shift, it is reasonable to interpret the magnetic resonance at low temperatures as an antiferromagnetic resonance with very small anisotropy field. For the alloy with 4.3 at.% Mn, $H_c=2400$ Oe at 1.2°K. The alloy with 4.3 at.% Mn shows the onset of the growth of an anisotropy field at about 60°K, which is considered to indicate the fix of the domain boundaries between antiferromagnetic and ferromagnetic domains. This temperature should be able to define as T_N. The origin of the anisotropy field is supposed to come from the molecular field $\lambda_{FA}M_F\alpha$ which is due to the interdomain exchange interaction between an antiferromagnetic and a ferromagnetic domains. Here λ_{FA} is the effective interdomain coupling coefficient, M_F is the magnetization of ferromagnetic domain, and α is a positive quantity that ranges from 0 to 1 depending on the exact conditions at the domain boundaries. According to Kouvel's model, the α parameter is smaller in a metastable condition cooled in a magnetic field than in a stable condition cooled in zero magnetic field. The inhibition of the shift observed by Griffiths for the alloys cooled in a magnetic field is qualitatively explained by this model. For the alloy with 4.3 at.% Mn, the temperature dependence of the shift shows the growth of the ferromagnetic moment below the ferromagnetic Curie temperatures distributed over the wide range between about 60 and 0°K. The anisotropy field $\lambda_{FA}M_F\alpha\simeq 10$ Oe at 1.2°K for the 4.3 at.% Mn alloy, assuming $H_E=\lambda_AM_A=3\times10^5$ Oe from the simplest molecular-field theory. The remanent moment per Mn atom is $\sim 0.6\mu_B$ at 1.8°K[2] when the alloy is cooled in a magnetic field. $\lambda_{FA}\alpha\sim 15$ and $\lambda_A\sim 10^4$, assuming $M_F=10^{-1}SN\mu_B$ and $M_A=\frac{1}{2}SN\mu_B$. Here S is the spin of Mn atom and N is the number of Mn atoms in a unit volume. α will be an order of 10^{-2}–10^{-3}. A large anisotropy field in an antiferromagnetic domain assumed by Kouvel is not expected from the ESR. The origin of a large anisotropy field which fixes the ferromagnetic moment at low temperatures is unknown.

ACKNOWLEDGMENTS

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