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Electron spin resonance study in ternary metallic spin-glass $Cu_{88-x}Mn_{12}T_x$ alloys

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Abstract. Magnetisation and ESR studies on $Cu_{88-x}Mn_{12}T_x$ spin-glass alloys have been performed over the temperature range from 4.2 to 300 K where the concentration x of the non-magnetic impurity T (≡Ni or Au) ranges from 0.5 to 2 at.%. The effects of the non-magnetic impurities on the temperature dependences of the anisotropy energy, linewidth and resonance shift have been investigated. A large reduction in the degree of bottleneck and a rapid increase in the effective relaxation rate with increasing temperature for samples containing Au have been observed. The inverse susceptibility can be used to describe the ESR linewidth data.

1. Introduction

The ESR of dilute metallic alloys was studied many years ago. For very dilute alloys and for temperatures above the freezing temperature, the Korringa mechanism and bottleneck effect are effective (Hasegawa 1959). Rapid increases in the ESR linewidth and line shift with decreasing temperature have been observed in Cu–Mn (Okuda and Date 1969, Hoekstra *et al* 1982) and in Au–Mn (Vaknin *et al* 1981) spin-glass alloys. The hydrodynamic model (Schultz *et al* 1980, 1981, Henley *et al* 1982) connects the observed shifts nicely to the anisotropy as found in magnetisation and ESR experiments.

Prejean *et al* (1980) found that the addition of non-magnetic impurities with strong spin–orbit coupling (Au and Pt) sharply increases the anisotropy. They have shown that the increase in the anisotropy can be accounted for by the Dzyaloshinski–Moriya interaction (Dzyaloshinski 1958, Moriya 1960), which causes the enhancement of the spin–orbit scattering of the conduction electrons by the ternary impurity.

The explanation of the temperature dependence of the linewidth is less clear, since there seems to be a strong dependence on the spectrometer frequency. Several attempts have been carried out to calculate ΔH and its extrapolation to zero frequency. Becker (1982) and Saslow (1984) developed a general theory for the temperature and the frequency dependences of the shift and linewidth, both thought to be due to the anisotropy. Mahdjour *et al* (1986) suggested that the linewidth is not only frequency dependent but also field dependent, and hence not the temperature T but the internal temperature H/M should be used as a parameter. This suggestion indeed removes the apparent frequency dependence.

In this paper, magnetisation and ESR investigations on $Cu_{88-x}Mn_{12}T_x$ spin-glass alloys have been performed with the aim of studying the effects of including different

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concentrations of the non-magnetic impurities Au and Ni on the bottleneck, anisotropy energy and relaxation of the spin glasses.

2. Experiment

2.1. Preparation of samples

The master $Cu_{88}Mn_{12}$ sample was obtained by melting together appropriate amounts of the constituent elements by arc melting under an Ar atmosphere. The glowing buttons were quenched to room temperature in the arc furnace. The master $Cu_{88}Mn_{12}$ sample was cleaned in dilute HNO_3 and divided into several parts. Using these parts we prepared the ternary alloys with 2 at.% Au and 2 at.% Ni by arc melting in the same way as described above. The other alloys with lower concentrations of Au and Ni were prepared by diluting the alloys having higher concentrations of Au and Ni with $Cu_{88}Mn_{12}$.

X-ray analysis showed that all the samples have an FCC structure with no indication of segregation. The homogeneity and concentration of the samples were determined by microprobe analysis and checked by comparing the value of T_f in Cu–Mn with those given in literature (Mydosh and Nieuwenhuys 1980).

All our samples were spherical and of diameter 2.8 mm to obtain the maximum field homogeneity.

2.2. Measurements

ESR measurements were performed at 9.4 GHz. Samples were cooled using a ^{4}He gas flow cryostat. The temperature was measured using an Au–Fe–chromel thermocouple in contact with the sample. The resonance signals have the usual characteristics of dilute magnetic alloys with $A/B = 2.5$ (the ratio of the maximum to the minimum height of the absorption derivative line) in the paramagnetic region (Peter *et al* 1976).

The spectrometer was controlled with a personal computer. A vibrating-sample magnetometer was used to measure the magnetisation. The magnetic field lies in the same vertical direction as the vibrating sample and is produced from superconducting coils. The freezing temperature T_f of the sample was determined from the cusp in the low-frequency zero-field-cooled AC susceptibility measurements.

3. Results and discussion

3.1. Magnetisation

The freezing temperature T_f of 52 K was found to be approximately independent of the addition of the non-magnetic impurity Ni or Au to $Cu_{88}Mn_{12}$.

Figure 1 shows a complete hysteresis cycle at 4.3 K for $Cu_{88}Mn_{12}$ and samples with different concentrations of Au and Ni. All recorded hysteresis loops were started at the cooling field of 5 kOe; the field was then swept to −5 kOe and back again to 5 kOe, which is similar to the field sweep in the ESR measurements. The total magnetisation M in the field-cooled state can be represented by the linear equation $M = \sigma + \chi(T)H$, where σ is the thermoremanent magnetisation and $\chi(T)$ is the reversible susceptibility determined from dM/dH outside the hysteresis loop. The values of σ, χ and the field on reversal of magnetisation which can be obtained from the hysteresis loop are needed for

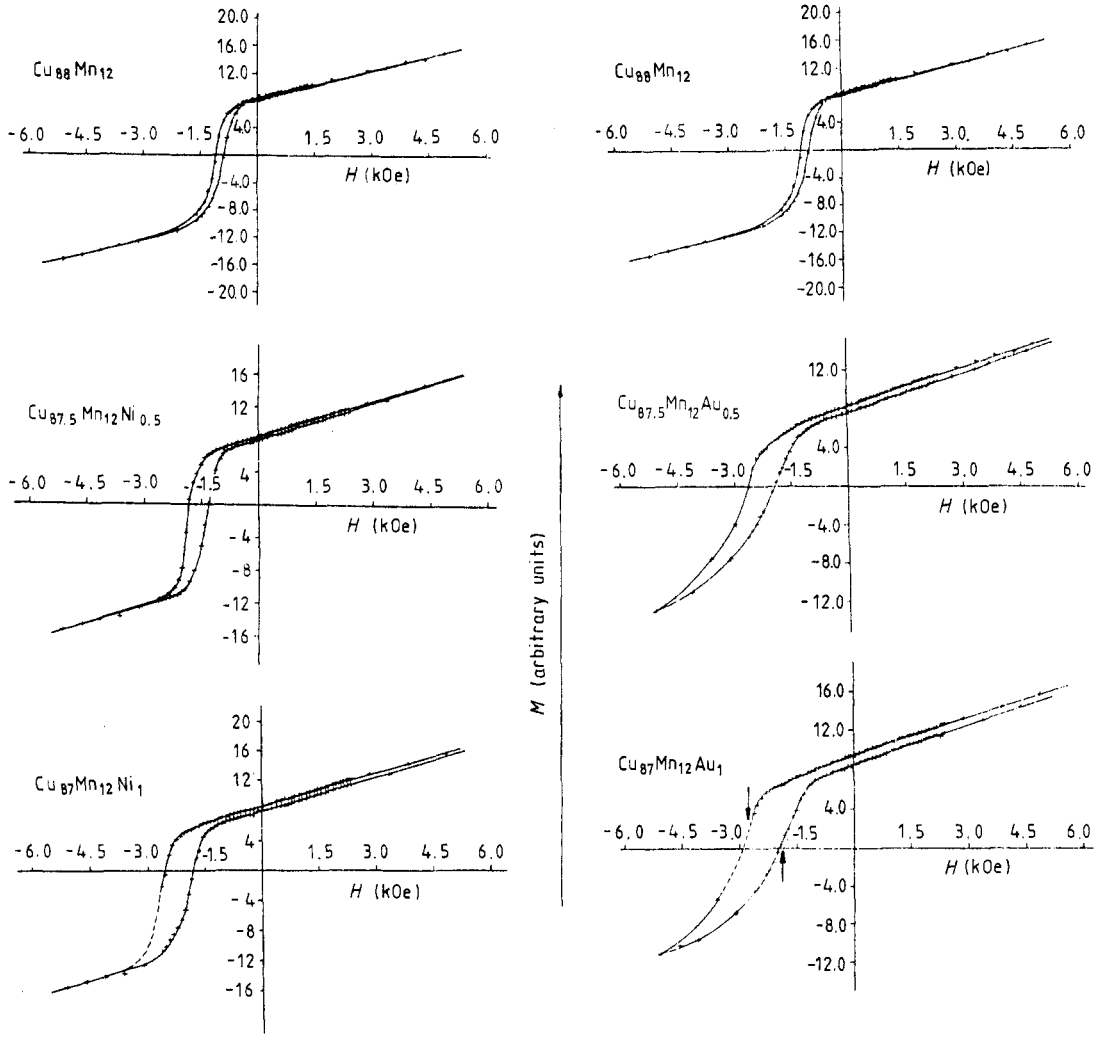

Figure 1. Hysteresis loops measured at 4.2 K for $Cu_{88}Mn_{12}$ and alloys with Au and Ni for several Au or Ni concentrations cooled in a field of 5 kOe from 300 to 4.2 K. The arrows represent the field flip-down and field flip-back.

analysis of the ESR data. It is clear from figure 1 that the remanent magnetisation is independent of the addition of the non-magnetic impurities (Au and Ni), which indicates that the spin glass remains the same, except for the anisotropy.

From a study of Cu–Mn alloys, Hippert and Alloul (1982) showed that the anisotropy energy is related to both the unidirectional anisotropy K_1 and the uniaxial anisotropy K_2 by the relation $E_{\text{anis}} = -K_1 \cos\theta + \frac{1}{2}K_2 \sin^2\theta$, where θ is the angular displacement of the remanent magnetisation.

The anisotropy parameters K_1 and K_2 can be deduced from the hysteresis loop (Alloul and Hippert 1983, Hoekstra 1985) where the centre of the loop, i.e. H_{av}, is calculated to be $2K_1/\sigma$, while the hysteresis width $2\,\Delta H$ is calculated to be $2K_2/\sigma$. The

Table 1. Magnetisation parameters measured from hysteresis loops at $T = 4.2$ K after field cooling at 5 kG.

	$Cu_{88}Mn_{12}$, $x = 0$	$Cu_{88-x}Mn_{12}Au_x$			$Cu_{88-x}Mn_{12}Ni_x$		
		$x = 0.5$	$x = 1$	$x = 2$	$x = 0.5$	$x = 1$	$x = 2$
χ (10^{-4} emu g^{-1})	1.2	1.17	1.33	1.2	1.25	1.14	1.17
σ (emu g^{-1})	0.768	0.786	1.0	0.735	0.76	0.76	0.76
$2\Delta H$ (Oe)	214	657	1000		500	714	1000
H_{av} (Oe)	−967	−2293	−2500		−1607	−2143	−3428
$H_{\downarrow}$ (Oe)	−1071	−2643	−3000	−4940	−1857	−2535	−3930
K_1 (erg g^{-1})	742	1800	2922		1220	1542	2567
K_2 (erg g^{-1})	82	258	584		190	250	370
H_{res} [a](Oe)	2671	1615	1260		2180	1750	803
H_{res} [b](Oe)	2730	1855	1295		1600	1792	832

[a] The fields for resonance calculated from the hydrodynamic theory using the magnetisation parameters χ and σ.

[b] The observed ESR resonance field after field cooling at 5 kOe.

field where the 'flip-down' occurs is $H_{\downarrow} = H_{av} + \Delta H = (K_1 + K_2)/\sigma$, whereas the 'flip-back' occurs at $H_{\uparrow} = H_{av} - \Delta H = (K_1 - K_2)/\sigma$.

It was found that the Au impurity has a large effect on the unidirectional anisotropy, as a result of the spin–orbit scattering of the conduction electrons by the Au impurity (Prejean *et al* 1980, Fert and Levy 1980, Levy and Fert 1981). Table 1 represents the magnetisation parameters χ, σ, K_1 and K_2 deduced from the hysteresis loops at 4.3 K.

3.2. *ESR*

The data on the linewidths for some of our samples are presented in figure 2. The results for zero-field-cooled samples coincide with the field-cooled data for 40 K $< T <$ 300 K. Thus the analysis of the data should be divided into two temperature regions: those at high temperatures and those at low temperatures.

3.2.1. Linewidth at high temperature $T > 3T_f$. In this region the linewidth varies linearly with temperature, satisfying the relation $\Delta H = a + bT$, where a is the so-called residual linewidth and b is a measure of the Korringa bottleneck thermal broadening. The values of b (the slopes of the linear plots) were found to be independent of the Au or Ni concentrations between 0.5 and 2 at.%. However, a marked dependence on the type of scatterer (Ni or Au) was noticed and values of the parameter b are as follows: $Cu_{88}Mn_{12}$, 2.55 G K^{-1}; $Cu_{88-x}Mn_{12}Ni_x$, 3.2 G K^{-1}; $Cu_{88-x}Mn_{12}Au_x$, 4.75 G K^{-1}. These observations indicate that the bottleneck is still present, but partially open by the addition of Au or Ni. The strength of the bottleneck is governed by the ratio δ_{eL}/δ_{ei}, where δ_{eL} and δ_{ei} represent the relaxation rates of the conduction electrons due to the lattice and magnetic ions, respectively. A decrease in bottleneck can be achieved either by a decrease in the concentration of the magnetic ions or by the addition of spin–orbit scatterers to the alloy (Zomack *et al* 1983).

The values obtained for the residual width a (ΔH at $T = 0$), as shown in figure 2, appear to be all negative which is rather unphysical. Such negative values of a are often observable in binary spin glasses, while the addition of non-magnetic impurities produces

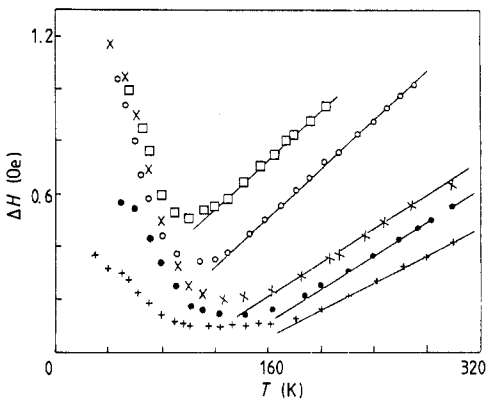

Figure 2. Temperature dependence of the ESR linewidth for the positive field signal in the $Cu_{88-x}Mn_{12}T_x$ system: □, $Cu_{86}Mn_{12}Au_2$; ○, $Cu_{87}Mn_{12}Au_1$; ×, $Cu_{86}Mn_{12}Ni_2$; ●, $Cu_{87}Mn_{12}Ni_1$; +, $Cu_{88}Mn_{12}$.

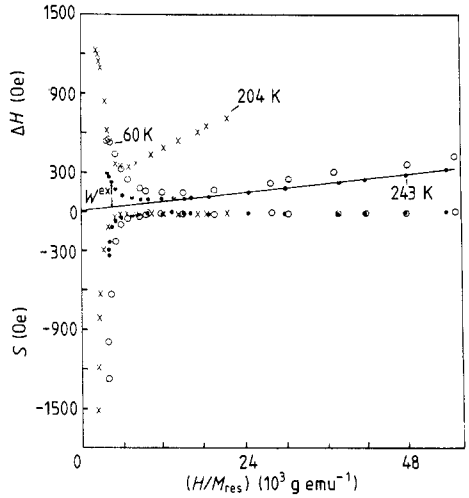

Figure 3. ESR linewidth and resonance shift at 9.44 GHz as a function of $(H/M)_{res}$ for $Cu_{88}Mn_{12}$ (●), $Cu_{87}Mn_{12}Ni_1$ (○) and $Cu_{87}Mn_{12}Au_1$ (×): —, the Korringa law with positive residual linewidth.

Table 2. The residual linewidths a, a_0 and a^* for the $Cu_{88-x}Mn_{12}T_x$ system measured from the ESR linewidth as functions of T, $T-\Theta$ and χ^{-1}, respectively.

	$Cu_{88}Mn_{12}$, $x=0$	$Cu_{88-x}Mn_{12}Ni_x$			$Cu_{88-x}Mn_{12}Au_x$		
		$x=0.5$	$x=1$	$x=2$	$x=0.5$	$x=1$	$x=2$
a (Oe)	−340	−440	−405	−318	−325	−215	−10
a_0 (Oe)	−10	35	70	155	90	185	370
a^* (Oe)	5	10	16	26	63	124	244

a positive residual width (Zomack *et al* 1983). This discrepancy in the sign of the residual width for our ternary alloys can be interpreted as arising from the large positive Curie–Weiss temperature Θ resulting from the Mn concentration used in Cu ($\Theta > 100$ K).

Table 2 gives the values of the residual linewidth a for the different Ni and Au concentrations. It is shown that Au increases the residual width more rapidly than Ni does in $Cu_{88}Mn_{12}$.

The results obtained from plotting the linewidth data as a function of $T-\Theta$ using the equation (Zomack *et al* 1983)

$$\Delta H = a_0 + b(T-\Theta) = (a_0 + b\Theta) + bT \tag{1}$$

give rise to a positive value of the residual linewidth a_0 for all samples except $Cu_{88}Mn_{12}$ (see table 2).

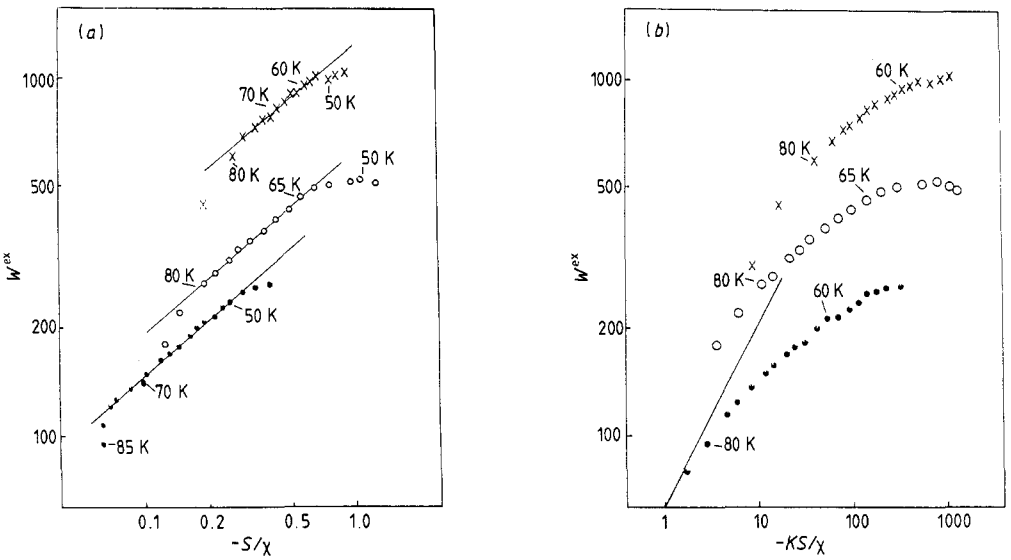

Figure 4. Log–log plots of W^{ex} (*a*) as a function of $-S/\chi$ and (*b*) as a function of $-KS/\chi$ for $Cu_{88}Mn_{12}$ (●), $Cu_{87}Mn_{12}Au_1$ (×) and $Cu_{87}Mn_{12}Ni_1$ (○). (*a*) is in the temperature region $T_f \leq T \leq 1.5T_f$. In (*b*) the full line corresponds to a slope of 0.5.

Following Mahdjour *et al* (1986), the high-temperature linewidth can be interpreted according to

$$\Delta H = a^* + b^*T^* \tag{2}$$

where T^* is the internal temperature equal to H/M. In figure 3 we have plotted the linewidth and also the line shift as functions of H/M measured at the field for resonance where the temperature is an explicit parameter. It is clear that ΔH obeys equation (2) and a^* is positive in all cases; this is a logical consequence of the fact that H/M automatically incorporated the Curie–Weiss behaviour of the magnetic susceptibility.

3.2.2. Linewidth at low temperatures ($T_f < T < 2T_f$). At temperatures below $2T_f$ the linewidth strongly increases with decreasing temperature.

Using Mahdjour's approach, the excess linewidth can be written as

$$W^{ex} = \Delta H - a^* - b^*T^*. \tag{3}$$

The relation between the excess linewidth W^{ex} and the line shift S was proposed as a half-power law as shown from the following equations:

$$W^{ex} \propto [-S/(\chi\omega/\gamma)]^{0.5} \tag{4}$$

and

$$W^{ex} \propto [-KS/(\chi\omega/\gamma)]^{0.5} \tag{5}$$

where ω/γ represents the resonance field at $g = 2$.

Equation (4) holds when the effective relaxation rate is greater than the spectrometer frequency (Salamon and Herman 1978, Salamon 1979), while equation (5) is correct if the spin-triad relaxation is more rapid than ω (Becker 1982, Saslow 1984).

In figure 4(*a*), W^{ex} has been plotted as function of $-S/\chi$ and in figure 4(*b*) as a function of $-KS/\chi$. For the $-S/\chi$ plot it is clear that the experimental points for $Cu_{88}Mn_{12}$,

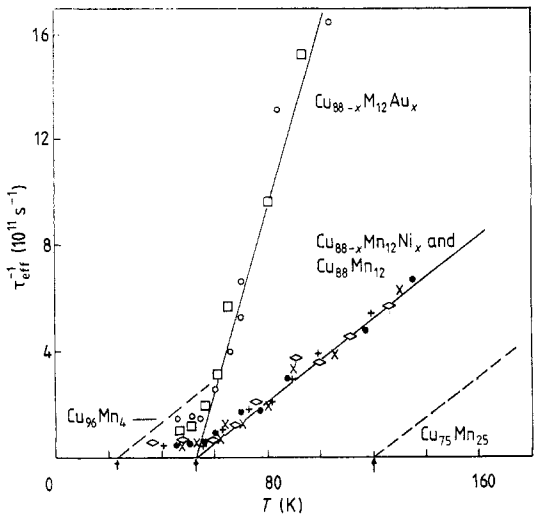

Figure 5. Temperature dependence of the effective relaxation rate determined from equation (6) for $Cu_{88}Mn_{12}$ and alloys with Ni and Au: ---, data of Salamon and Herman (1978). The arrows indicate the freezing temperature.

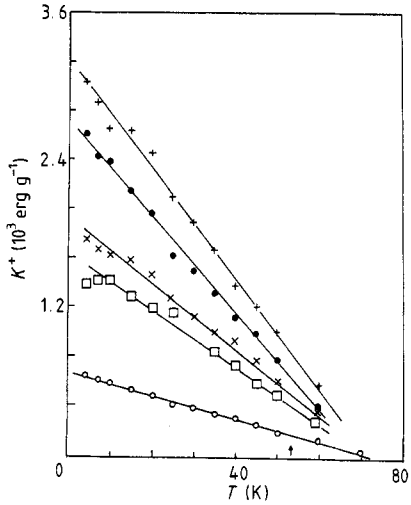

Figure 6. The sum of the anisotropy parameters K^+ against T for the $Cu_{88-x}Mn_{12}T_x$ system, calculated from the ESR line shift and the magnetisation parameters σ and χ: ○, $Cu_{88}Mn_{12}$; □, $Cu_{87.5}Mn_{12}Ni_{0.5}$; ×, $Cu_{87}Mn_{12}Ni_1$; ●, $Cu_{86}Mn_{12}Ni_2$; +, $Cu_{87}Mn_{12}Au_1$.

$Cu_{87}Mn_{12}Ni_1$ and $Cu_{87}Mn_{12}Au_1$ show good agreement with the half-power law proposed by Salamon and Herman (1978). On the other hand, for $-KS/\chi$ the experimental points deviate from the full line of slope 0.5. This means firstly that the linewidth and the line shift are indeed related, indicating a dynamic process, and secondly that the model of Salamon and Herman (1978) best describes the freezing of spin motion in our spin-glass alloys.

According to the model of Salamon and Herman (1978), the effective relaxation rate can be represented as

$$\tau_{\text{eff}}^{-1} = g/(T_2\,\Delta g) \tag{6}$$

where T_2 is the spin–spin relaxation time (measured from the linewidth data) and Δg is the g-shift.

In figure 5 we have plotted the average values of the effective relaxation rate for our samples as a function of temperature together with the data for $Cu_{96}Mn_4$ obtained by Salamon and Herman (1978). It is shown that the relaxation rate vanishes at T_f, in agreement with the model Salamon and Herman (1978).

It can also be established from figure 5 that the addition of Ni impurities has no effect on the relaxation process since the slope is roughly equal to that of binary Cu–Mn alloys, while Au impurities (of large spin–orbit coupling constant) lead to a rapid increase in the slope. This is probably due to the increase in the conduction electron lattice relaxation rate δ_{eL} resulting from the addition of non-magnetic impurities to the Cu–Mn alloys.

3.3. Anisotropy

The sum of the anisotropy parameters referred to as K^+ (for parallel applied and cooling fields) can be determined using the ESR line shift S and the magnetisation parameters χ

and σ from the hydrodynamic theory of spin-glasses (Schultz *et al* 1980, 1981, Henley *et al* 1982) as

$$K^+ = S[\chi(\omega/\gamma) + \sigma]. \tag{7}$$

Both the magnetisation and the ESR measurements are recorded under the same sweep and cooling field conditions. Figure 6 shows the temperature dependence of K^+. It is clear that the anisotropy K^+ decreases linearly with increasing temperature and equals zero at about $1.5T_f$. In contrast the static anisotropy measured from the displaced hysteresis loop shows a zero value at about $0.6T_f$ (El-Sayed 1988) when the remanence magnetisation is zero. Such a difference can be understood from equation (7), by noting that K^+ has a non-zero value when $\sigma = 0$. This observation is in accord with the fact that the isothermal remanent magnetisation (σ in the zero-field-cooled case) exhibits anisotropy effects as measured via torque experiments (Iwata *et al* 1970, Hippert and Alloul 1982).

The temperature dependence of K^+ as shown in figure 6 is in agreement with the experimental equation deduced by Schultz *et al* (1980) for Cu–Mn and alloys with Ni:

$$K^+(T) = K(0)(1 - \beta T/T_f) \qquad \text{with } \beta = 0.74.$$

The reduced anisotropy energy $K(0)$ takes the form

$$K(0) = aC_{Mn}^2 + b_i C_{Mn} C_i$$

where a and b are the concentration coefficients for Mn and the non-magnetic impurity, respectively. It appears that our data for Ni and Au alloys are consistent with the above equation with $a = 48$ erg cm^{-3} (at.% Mn)$^{-2}$, $b_{Ni} = 880$ erg cm^{-3} (at.% Ni)$^{-2}$ and $b_{Au} = 1940$ erg cm^{-3} (at.% Au)$^{-2}$. Such values are less than expected from the low-Mn-concentration results but consistent with those measured from magnetisation. This can be attributed to metallurgical effects (Hoekstra 1985).

4. Conclusions

Measurements carried out on the ternary metallic spin-glass $Cu_{88-x}Mn_{12}T_x$ alloys revealed a large increase in the anisotropy in alloys with Au and a moderate increase for those containing Ni. This difference can be correlated to the different spin-flip scattering and spin–orbit coupling constants of Au and Ni in Cu.

The difference in the resonance shift for signals recorded with the field parallel and antiparallel to the cooling field is explained in terms of induced unidirectional and uniaxial anisotropies. The temperature dependence of the anisotropy for the positive field signal K^+ reaches zero near $1.5T_f$.

The temperature dependence of the ESR linewidth against the inverse susceptibility at resonance field showed that the excess linewidth, which is due to the spin-glass freezing, could be extracted and is proportional to the square root of the ESR line shift over the temperature range from T_f up to $1.5T_f$, in agreement with the prediction of Salamon and Herman (1978).

Finally a rapid increase in the effective relaxation rate with increasing temperature in Cu–Mn–Au samples was observed.

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