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Specific Heat of $Dy_{.40}$ $Cu_{.37}$ $Y_{.23}$ Amorphous Alloy at Low Temperatures

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الحرارة النوعية للسبيكة $Dy_{.40}$ $Cu_{.37}$ $Y_{.23}$ في درجات الحرارة الواطئة

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خلاصة : تم في هذا البحث دراسة الحرارة النوعية في درجات الحرارة الواطئة للسبيكة العشوائية المغناطيسية $Dy_{0.40}Cu_{0.37}Y_{0.23}$ في مدى درجات الحرارة 2 K إلى 50 K. إذ تم حساب المساهمة المغناطيسية في الحرارة النوعية وتغيرات الانتروبي المغناطيسي ودرجة حرارة التحول في الطور المغناطيسي والعزم المغناطيسي المؤثر.أظهرت الحرارة النوعية المغناطيسية قمة عريضة مرتكزة عند درجة حرارة، T_m مساوية تقريبا إلى 28 K متبوعة بتأثير شوتكي. إن قيمة T_m أعلى من قيمة T_f والمساوية إلى 23.5 K والمقاسة من التأثرية المغناطيسية. كانت قيم الانتروبي المغناطيسي المحسوبة بين 0 K إلى T_m مساوية تقريبا إلى 84 % من قيمة الانتروبي المغناطيسي العظمى المحسوبة نظريا. تتفق تصرفات هذه السبيكة العشوائية مع تصرفات السبائك العشوائية المكثفة للعناصر الأرضية النادرة.

ABSTRACT: The low temperature specific heat of the magnetic $Dy_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy have been investigated in the temperature range 2 to 50 K. The magnetic contributions to the specific heat, magnetic entropy changes, ordering temperatures and the effective magnetic spin have been estimated for this magnetic amorphous alloy. The magnetic specific heat show broad anomaly at a certain temperature, T_m of about 28 K. The value of T_m is higher than T_f (=23.5 K) determined from low field ac susceptibility measurements. The magnetic entropy changes between 0 K and T_m are estimated to be 84 % of the maximum theoretical value. The behaviors of this amorphous alloy agree quit well with those of condensed rare earth amorphous systems.

KEYWORDS: Specific Heat, Amorphous Alloys, Dysprosium Amorphous Alloys.

1. Introduction

Crystal field effects are likely to be well-defined in amorphous rare earth (RE) alloys. The topological disorder in this amorphous alloy results in a competition in sign exchange interactions together with random uniaxial crystal fields with the local easy axis of magnetic anisotropy varying from site to site (Coey, 1978; Harris *et al.*, 1979). The low temperature specific heat of rare earth magnetic amorphous alloys appears to posses intrinsic features such as the well defined sharp anomaly in the low field ac susceptibility at a certain temperature, T_f, which is a function of the magnetic element, a broad maximum in the specific heat at a temperature, T_m, and specific heat linear term in T at low temperatures. Moreover, characteristics contributions to the specific heat are expected in the paramagnetic phase resulting from the crystal field excitations. The low temperature specific heat results of some rare earth metals and alloys show another contribution to the specific heat arising from the hyperfine nuclear magnetic effects (Garoche *et al*., 1980).

Measurements of the specific heat of $Pr_{21}Ag_{79}$, $Sm_{21}Ag_{79}$ and $Lu_{21}Ag_{79}$ amorphous alloys reported by (Garoche *et al*., 1980) are characterized by a large and nearly temperature independent term down to very low temperatures. These behaviors have been attributed to the low energy crystal field excitations associated with the distribution of the asymmetry parameter of the crystalline electric field effects.

Values of the magnetic entropy changes, which have been usually estimated between 0 K and T_f and T_m are usually less than the maximum magnetic entropy expected theoretically. This means that effective spin value is less than the maximum value expected for pure metals and there is still considerable amount of magnetic order even at temperatures higher than T_f and T_m. The specific heat and ac susceptibility of the amorphous $Gd_xCu_{0.37}Y_{0.63-x}$ ($0<x<0.63$) have been studied at low temperature (Mohammed *et al*., 1986). This investigation showed the spin glass nature for $x<0.35$ for Gd. The magnetic amorphous $Dy_{0.40}Cu_{0.37}Y_{0.23}$ alloy exhibits low cusp in its low field ac susceptibility as shown in Figure 1, indicating spin glass phase transition to the paramagnetic phase (del Moral *et al*.,1986). Theoretical calculations of Debye temperature, lattice specific heat and the spin glass ordering temperatures in the magnetic $RE_{0.33}Cu_{0.67}$, $RE_{0.33}Al_{0.67}$ and $RE_{0.33}Ag_{0.67}$ amorphous alloys have been reported (Mohammed *et al*., 1994). Spin glass like behavior and low temperature specific heat have been investigated for bulk amorphous Er_xNi_{1-x} (x=0.33, 0.50 and 0.80) alloys prepared by high rate direct current sputtering (Hattori *et al*., 1995). The specific heat parameters of the magnetic Er-Cu-Y and Ho-Cu-Y amorphous alloys had been investigated in the temperature range 0 K to 50 K (Mohammed K. A. to be published).

2. Experimental procedure

The phase diagram of the crystalline binary Cu-Y alloys shows that the deepest eutectic point occurs at about 33 at % Cu. It has been reported (Rainford *et al*., 1982). that a 37 at % Cu is marginally better for glass formation than 33 at % Cu. Accordingly, copper proportion was fixed at 37 at % in this sample. Prior to preparing ribbons in the amorphous state polycrystalline alloys were prepared by melting together appropriate quantities of Dy, Cu and Y of 99.99% nominal purity, which were supplied by rare earth products Ltd. The alloys were prepared in an arc furnace in a high purity (99.999%) reduced argon atmosphere. The alloy was turned and remelted many times to promote homogeneity. The loss in the total mass after alloying was less than 0.1 %. The production of the amorphous ribbons method was the well tried melt spinning technique, which is quite similar to that described by Liebermann *et al*. (1976). In this method typically about half a gram of an alloy is melted by rf induction in a quartz crucible and immediately expelled under pressure onto a rapidly rotating massive copper wheel, which cools the melt sufficiently rapidly for amorphous samples to be produced. The crucible was about 5 to 10 cm long and 9 to 10 mm in diameter with an orifice of about 1mm diameter at its bottom end. High purity (5N) argon gas at pressure of 5 to 10 psi was used to force the molten stream through the hole in the bottom of the tube.

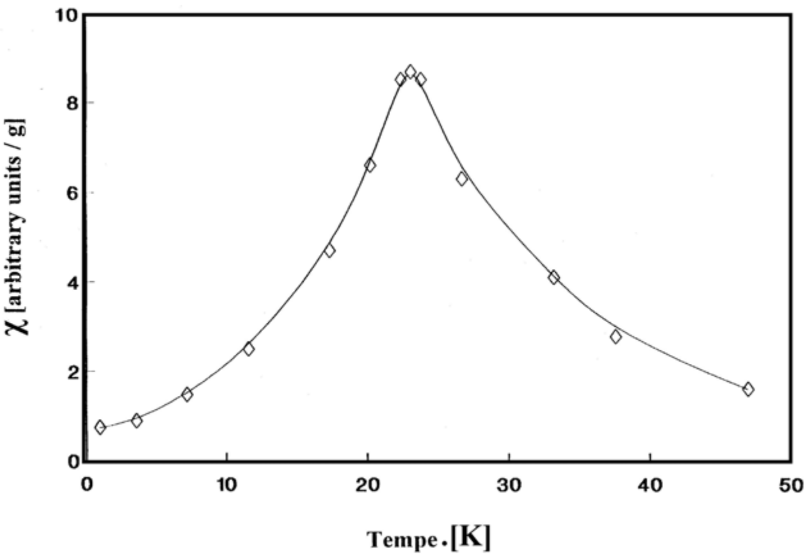

Figure 1. The ac susceptibility, χ versus temperature, T [Reference 5].

The space between the orifice and the surface of the copper wheel was between 1 and 3mm. The diameter of the copper wheel was 15 cm and the optimum speed of rotation was found to be approximately 4000 to 6000 rpm. The amorphous nature of the ribbons was checked by studying the x-ray diffraction using CuKα radiation. Normally no evidence of crystallite was observed. On the matter of testing samples for amorphicity, it is perhaps of interest to point out that we have found that in nearly every case an amorphous ribbon can sustain a sharp 180^o bend without fracture whereas the same operation will break ribbons with any trace of crystalline. This has been used to test the amorphicity of the very long length of ribbon required to form a satisfactory sample for heat capacity measurement. The heat capacity was measured using a modified adiabatic continues heating technique from 4.2 K to 50 K while the heat pulse technique has been used in the temperature range 1.5 K to 7 K. The accuracy of the measured temperature and the heat capacity were better than ± 3 mK and 1 % respectively (Lanchester *et al.*,1987).

3. Results and discussion

The total specific heat results, C_p, of the magnetic $Dy_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy are shown in Figure 2 as C_p versus temperature, T. Figure 2 also includes specific heat results of the non-magnetic $Lu_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy for comparison (Mohammed *et al.*, 1987). It is clear that there is no sharp transition in C_p at the ordering temperature, as observed in crystalline Dy metal and alloys (Lounassma *et al.*,1966).

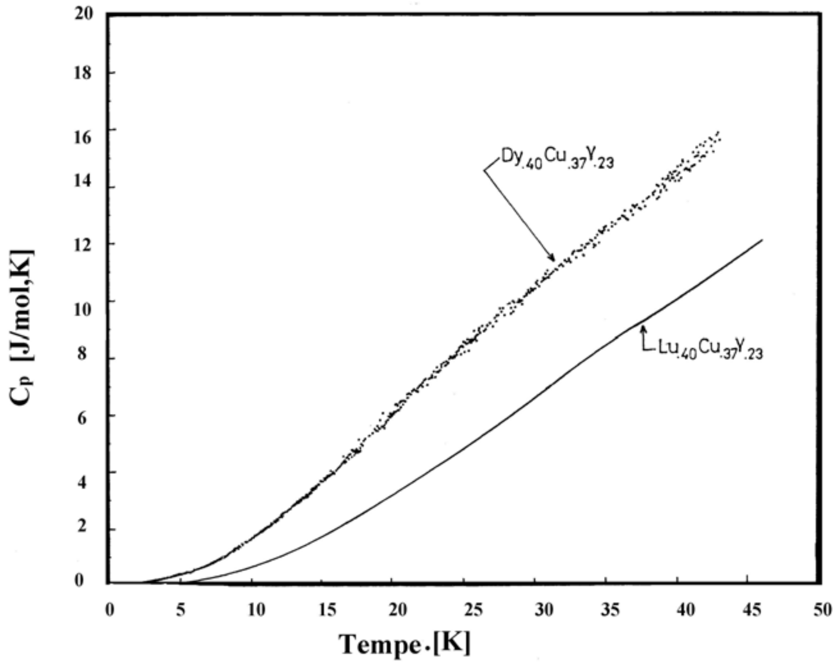

Figure 2. The specific heat C_p versus temperature, T.

The total specific heat C_p of the amorphous magnetic alloys can be written as ;

$$C_p = C_e + C_L + C_m \tag{1}$$

where C_e, C_L and C_m represent the electronic, lattice and magnetic terms respectively. C_m forms the major part of C_p for magnetic materials below their critical temperatures. An acceptable method to estimate values of the non-magnetic terms C_e and C_L is to use experimentally measured specific heat results of a similar but non-magnetic material (Lounassma *et al.*,1966). Therefore, the specific heat of the non-magnetic $Lu_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy can be considered to be the best alloy to represent the non-magnetic terms in the specific heat of the magnetic $Dy_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy. Fortunately, the experimental results of the reference materials do not need to be corrected for the atomic mass difference between the magnetic and non magnetic crystalline alloys because the average atomic weights are very similar and the difference does not affect the accuracy of such calculations.

The magnetic contribution to the specific heat can now be obtained simply by subtracting the specific heat of the non-magnetic $Lu_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy from the total specific heat C_p of the amorphous $Dy_{0.40}Cu_{0.37}Y_{0.23}$ alloy, i.e.;

$$C_m = C_{p(\text{Dy-Cu-Y})} - C_{p(\text{Lu-Cu-Y})} \tag{2}$$

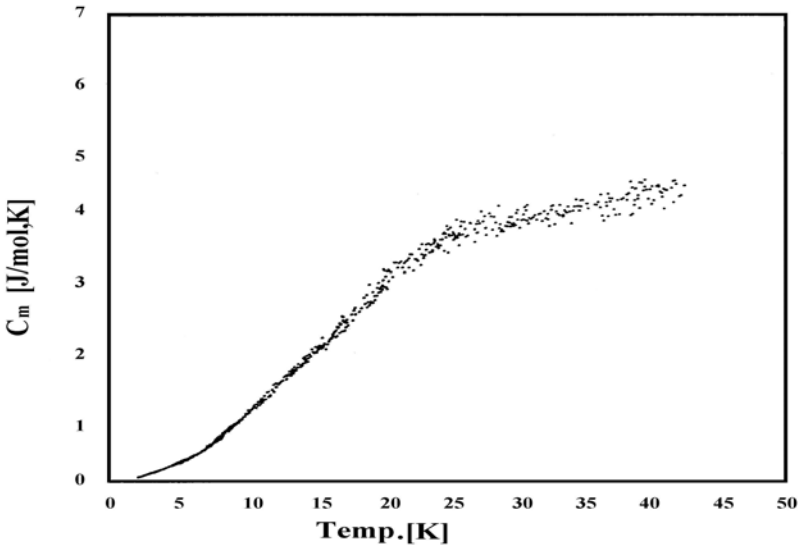

Figure 3. The magnetic specific heat, C_m versus temperature, T.

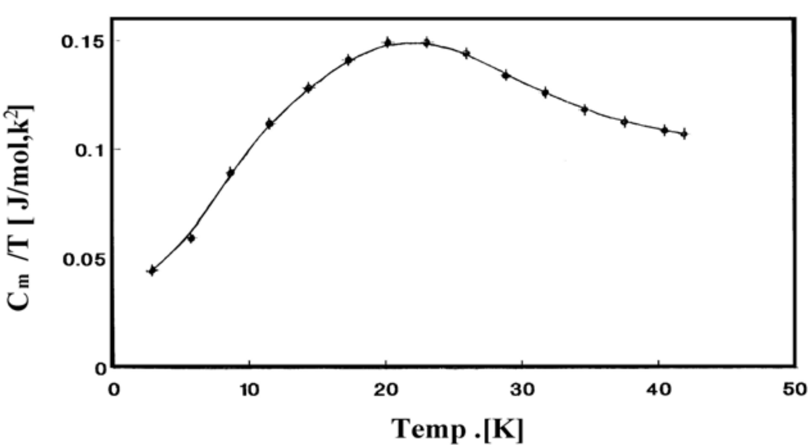

Figure 4. Cm / T versus temperature, T.

Values of C_m for this alloy are shown in Figure 3 as C_m versus T. This excess specific heats have been attributed to the magnetic effects in this magnetic alloy. It is clear that C_m shows clearly broad maximum centered at T_m=28±1 K. The value of T_m is about 1.1 times higher than the value of T_{sg}(=23.5 K)_ obtained from the low field ac susceptibility results (del Moral *et al.*,1986). Values of C_m/T versus T are shown in Figure 4.

The magnetic entropy changes, S_m, in the magnetic systems are usually related to the magnetic specific heat, C_m, through the following relation.

$$S_m = c\int \frac{C_m}{T} dT \quad (3)$$

where c represents the molar fraction of the magnetic metal in the alloy. The magnetic entropy changes, $S_m(T_m)$, in the alloy between 0 K and T_m have been determined by integrating the smooth C_m results between 0 K and T_m respectively. Moreover, the magnetic entropy changes (per mole) are theoretically related to the magnetic spin, J, of the magnetic element in the magnetic systems through another relation, which is

$$S_m = R\ln\left(2J+1\right) \quad (4)$$

where R is the gas constant. The numerically estimated values of the magnetic entropy changes, $S_m(T_m)$, between 0 K and T_m are shown in Table 1 together with the expected maximum entropy values obtained from equation (4) for J=15/2 for Dy ions. The ratio $S_m(T_m)/S_m(max)$ is equal to about 84 % . This indicates that the effective spin value is equal to about 6.3 rather than 15/2 in this alloy and the that there is still a considerable amount of magnetic order even at temperatures higher than T_f and T_m. This is very similar to the results of (Hattori *et al.*,1995) for the magnetic amorphous Er_xNi_{1-x} system, which shows magnetic entropy changes of about 45 % to 60 % of the theoretical maximum values with an effective spin value less than the 15/2 expected for Er ions.

The results of the low temperature specific heat of the amorphous Dy-Cu-Y alloy agree quite well with reported results for other magnetic amorphous systems such as $Pr_{21}Ag_{79}$, $Sm_{21}Ag_{79}$ and $Lu_{21}Ag_{79}$ amorphous alloys (Garoche *et al.*,1980), Gd-Y-Cu (Mohammed *et al.*, 1986), Tb-Y-Ni (Mohammed,1998), Er-Ni (Hattori *et al.*, 1995), Gd-Cu (Mohammed, 2002) and Er-Cu-Y and Ho-Cu-Y (Mohammed, to be published).

Table 1. Specific heat parameters of the magnetic $Dy_{.40}Cu_{.37}Y_{.23}$ amorphous alloy.

Calculated Parameters	$Dy_{.40}Cu_{.37}Y_{.23}$	
	Value	Ref.
T_f (K)	23.5	[del Moral, 1986]
T_m (K)	28 ± 1	This Study
T_m / T_f	1.1	
$S_m(T_m)$ (J/mol,K)	19.5 ± 1	
Spin (J)	15/2	
Effective Spin	6.3	
$S_m(max) = R\ell n\,(2J+1)$	23.56	
$S_m(T_m) / S_m(max)$ %	84 ± 2	

4. Conclusion

The specific heat of the magnetic $Dy_{0.40}Cu_{0.37}Y_{0.23}$ amorphous alloy has been investigated in the temperature range 2 to 50 K. The total specific heat does not show any clear changes at the ordering temperature, T_f, of the phase transition but the magnetic specific heat exhibits broad anomaly centered at T_m of about 28±1 K. The value of T_m is 1.1 higher than T_f determined from susceptibility measurements for the same alloy. The maximum magnetic entropy changes expected theoretically, $S_m(max)$, is calculated using the relation R ln(2J+1) for the spin value, J = 15/2 for a mole of Dy ions. The ratio of $S_m(T_m)/S_m(max)$ is equal to about 84 %. This gives an effective spin value equal to about 6.3 rather than 15/2.

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