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LETTER TO THE EDITOR

A new type of spin glass in spin-density-wave CrMn and CrSiMn alloys

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Abstract. Spin-density-wave (SDW) binary $Cr_{1-x}Mn_x$ ($x \ll 0.1$–4.6% Mn) and ternary (Cr + 1.3% Si)$_{1-x}Mn_x$ ($x = 0.17$ and 0.6% Mn) alloys are found to exhibit spin-glass behaviour, which differs however from that of a conventional spin glass in that the magnetic susceptibility $\chi(T)$ is essentially independent of temperature T between the low-temperature maximum and the Néel temperature T_N, and in that the temperature of the maximum is essentially independent of the Mn concentration. Comparison of binary and ternary alloys having the same Mn content shows that the nature of the maximum in $\chi(T)$ depends on whether or not the SDW is commensurate. A model is proposed that explains the increase in $\chi(T)$ at low temperature as resulting from pinning of the phase of the SDW to the Mn moments, which are frozen below T_N, causing frustration on the host Cr moments on the surfaces between the resultant SDW phase domains.

We have identified a new type of spin glass in binary and ternary alloys of Cr containing Mn. The chromium alloy system is the prototype of three-dimensional SDW systems, and has been extensively studied [1]. CrFe alloys are unique in this system in that Fe carries a moment that gives rise to a Curie–Weiss law for the temperature dependence of the magnetic susceptibility in the SDW phase [2, 3]. It is thus not surprising to find that antiferromagnetic (AFM) CrFe alloys, over a limited range of compositions close to the paramagnetic phase (and in the region of the phase diagram between the AFM and ferromagnetic phases), exhibit some characteristic features of spin-glass behaviour [4].

In CrMn alloys we observe spin-glass behaviour over a wide range of compositions from the most dilute ($x \ll 0.1\%$ Mn) to beyond $x = 20\%$ Mn (all concentrations are in atomic per cent). The anomalous temperature dependence of the susceptibility $\chi(T)$ in this system was first recorded by Maki and Adachi [5], who also observed hysteresis with respect to field cycling, which they attributed to weak ferromagnetism. The characteristic spin-glass feature of irreversibility with respect to temperature cycling in zero or finite field was not observed, however, because of the use of too large a magnetic field, $H = 2.4$ kOe.

We shall present in this letter experimental results for the temperature dependence of the magnetization $M(T)$ in small magnetic fields, and for the field dependence of $M(H)$ in fields up to 55 kOe, over the temperature range $T = 5$–400 K, for samples having a relatively low concentration, $x \leqslant 4.6\%$ Mn. For larger concentrations the behaviour becomes more complicated, and will be the subject of another paper.

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The temperature dependence of $M(T)$ in a constant small field (typically $H = 80$ Oe) of a sample cooled in zero field differs from that of a typical spin glass in that, following the characteristic peak, $M(T)$ falls rather sharply with increasing T and becomes constant above a 'pinning' temperature T_p. We believe that T_p is in fact the characteristic temperature of the spin glass, rather than that of the peak itself. Thus the increase of $M(T)$ below T_p is due to frustration of Cr moments at the interface between phase domains of the SDW centred on the frozen Mn moments. T_p changes hardly at all when the Mn concentration is varied from $x \ll 0.1$–4.6% Mn, in strong contrast to the close to linear relation between the freezing temperature and x in a typical spin glass. This behaviour follows naturally for our model, in which T_p is determined by the competition between the temperature-dependent magnetic anisotropy and interaction between the frozen moment on the Mn impurity atom and the SDW.

The reason for studying ternary alloys of Cr with 1.3% Si as well as Mn is that this concentration produces a commensurate SDW instead of the incommensurate SDW of pure Cr, and also causes a large increase in the amplitude of the SDW [1]. Thus comparison of binary and ternary alloys having the same Mn concentration provides information about the effects of both the commensurability of the SDW and the size of the magnetic moment on the Cr host lattice.

Ingots of the required composition weighing 70 g were melted in a vacuum-arc furnace in an argon atmosphere, and then crystallized on a water-cooled copper plate. They were remelted five times to achieve homogeneity, vacuum annealed for 24 h at a temperature of 1050 °C, and then quenched. The actual composition of some samples was determined by inductively coupled plasma atomic-emission spectroscopy, while that of the others was estimated from the Néel temperature T_N, with the knowledge of the dependence of $T_N(x)$ on Mn concentration x provided by the samples thus analysed. T_N was determined from the anomaly in the temperature dependence of the thermal equation [7].

Results for binary alloys $Cr_{1-x}Mn_x$, $x \ll 0.1$ and $x = 0.6$, 1.5, 3.1 and 4.6% Mn and for ternary alloys $(Cr + 1.3\%\ Si)_{1-x}Mn_x$, $x = 0.17$ and 0.6% Mn, are described here. The sample described as having $x \ll 0.1$% Mn contains only a trace of Mn, since its Néel temperature is not appreciably greater than that of pure Cr.

The magnetic susceptibility, defined as $\chi(T) = M(T)/H$, was measured with increasing temperature from $T = 5$ K, after cooling from $T > 100$ K in zero magnetic field, which is referred to as zero field cooled (ZFC), or in the measuring field, $30 < H < 1000$ Oe, which gives a field-cooled (FC) state of the sample. The magnetization was measured with a SQUID magnetometer from Quantum Design in San Diego.

In the field dependence measurements, which were all done at temperature 5 K, typically the virgin curve was first measured after cooling in zero field. The time dependence of the magnetization was measured at a few points in the subsequent hysteresis cycle to explore the possibility of relaxation effects.

We see from figure 1 that both binary CrMn and ternary CrSiMn alloys show two characteristic features of a spin glass, namely, the peak in the temperature dependence of the magnetic susceptibility $\chi(T)$ in the ZFC state, and the hysteresis when the sample is cooled in the measuring field (FC). In a typical metallic spin glass, in which the RKKY interaction between the magnetic impurity atoms is responsible for their frustration, the peak in the ZFC curve is identified as the freezing temperature T_f, which is proportional to the impurity concentration x for $x \lesssim 0.5\%$ Mn and then varies roughly as $x^{2/3}$ until clusters of impurity atoms dominate the behaviour for $x \gtrsim 10\%$. Furthermore, the decrease in $\chi(T)$ above T_f corresponds to the Curie–Weiss law that describes the thermal fluctuations of the moments on the impurity atoms [8].

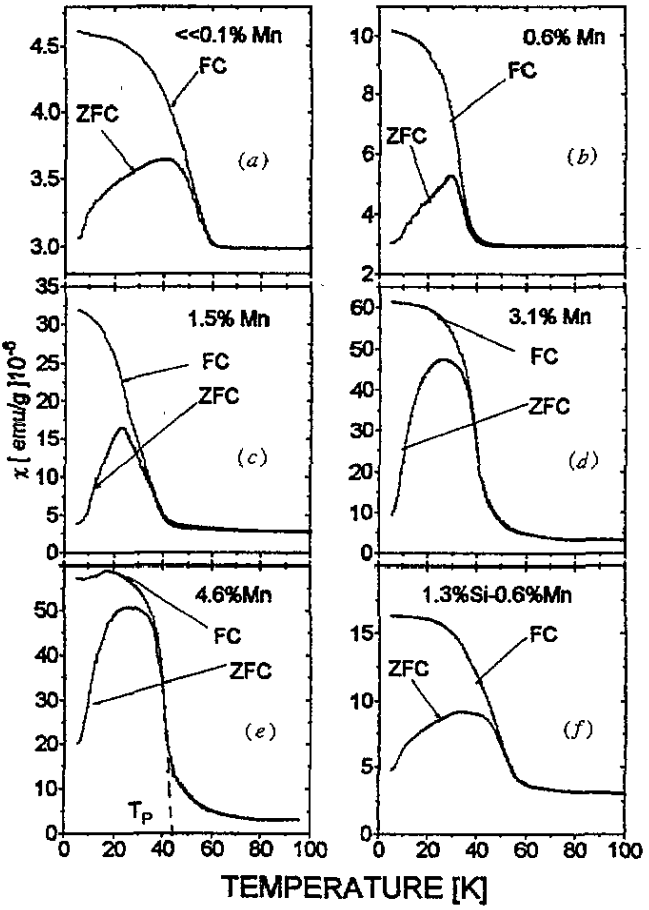

Figure 1. The temperature dependence of the magnetic susceptibility $\chi(T)$ determined from the magnetization in constant field, $H = 80$ Oe, for binary CrMn alloys and one ternary CrSiMn alloy. The ZFC and FC data are shown in each case. An extrapolation to zero χ of the ZFC curve, as illustrated by the dashed line for the $x = 4.6\%$ Mn sample, is used to define the pinning temperature T_p.

The behaviour in the $Cr_{1-x}Mn_x$ system is strikingly different. The pinning temperature T_p, whose definition is illustrated in figure 1(E), is essentially independent of x. On the other hand, the peak temperature shows no systematic variation with x, and, indeed, according to the model developed below to describe the behaviour of CrMn, has no particular significance. Furthermore, above T_p the susceptibility $\chi(T)$ soon becomes essentially independent of temperature T right up to the Néel temperature (or $T = 400$ K, if that is lower) for samples containing $x \leqslant 6.2\%$ Mn in our measurements, or $x \leqslant 10\%$ Mn in [5].

The nature of the peak changes from sharp for $x \leqslant 1.5$ to rounded for $x > 3.1\%$ Mn, the sample containing only a trace of Mn being anomalous in also having a rounded peak. The phase diagram of CrMn [7] indicates that this change in the nature of the peak may correspond to the change at $x \sim 2\%$ Mn from incommensurate to commensurate SDW at low temperatures. This idea is confirmed in the ternary CrSiMn alloy containing 0.6% Mn, in which the peak is rounded, as seen in figure 1(F), and the SDW is probably commensurate

at low temperature [1, 10].

In the FC state, the sample containing $x = 4.6\%$ Mn shows a small drop in $\chi(T)$ as seen in figure 1(E) at temperature decreases below about 20 K. This effect was reported also by Maki and Adachi [5] at about the same temperature, for compositions ranging from $x = 2.2$ to 14.7% Mn, but they employed a large measuring field, $H = 2.4$ kOe, so that there was no distinction between the FC and ZFC state, as we shall see below. The origin of this anomaly will be considered in a later publication.

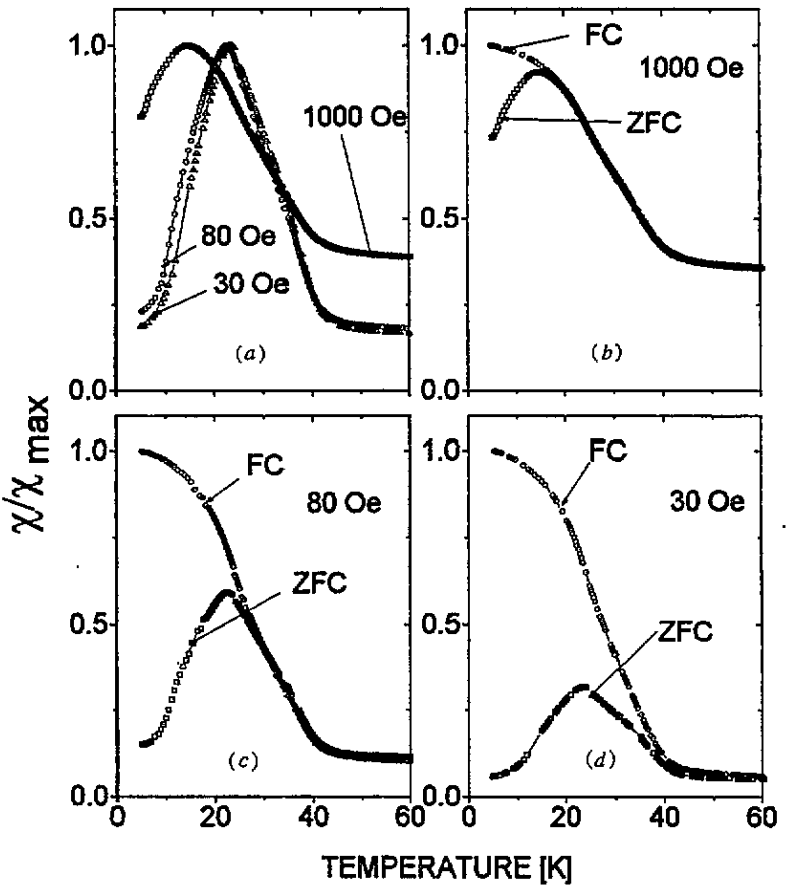

Figure 2. The temperature dependence of the magnetic susceptibility $\chi(T)$ in fields of 30, 80, and 1000 Oe for the Cr + 1.5% Mn sample in the FC and ZFC states: (A) in the ZFC state relative to the maximum value, and (B), (C), and (D) in both the ZFC and FC states relative to the maximum value, which occurs at the lowest temperatures in the FC state.

The hysteresis on temperature cycling between the ZFC and FC states becomes more pronounced as the measuring field H decreases, as seen in figure 2. For $H = 30$ Oe, the irreversibility limit where the ZFC and FC curves separate is essentially at the pinning temperature. The progressive decrease of the irreversibility limit as the field increases from 30 to 80 and 1000 Oe seen in figure 2 suggests that the failure to observe temperature hysteresis in previous studies [5] was due to the use of too large a measuring field,

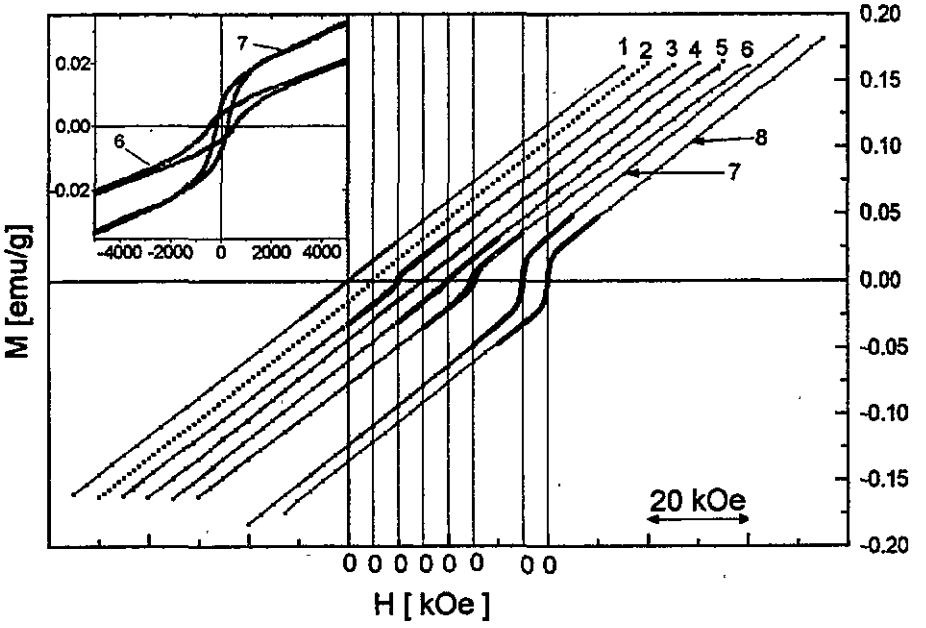

Figure 3. The magnetic field dependence of the magnetization $M(H)$ between $H = \pm 55$ kOe of $(Cr + 1.3\%\ Si)_{1-x}Mn_x$ alloys with Mn concentration (1) zero, (2) 0.17, and (3) 0.6% Mn, and of $Cr_{1-x}Mn_x$ alloys with (4) ≪0.1, (5) 0.6, (6) 1.5, (7) 3.1, and (8) 4.6% Mn.

$H = 2.4$ kOe. We note also from figure 2(A) that the peak in $\chi(T)$ for the ZFC state becomes more rounded at higher fields, while the peak temperature decreases.

The field dependence of the magnetization $M(H)$ is non-linear and exhibits hysteresis, as illustrated in figure 3. The parameters of the magnetic hysteresis are given in table 1. The coercive field H_c in our CrMn samples peaks at 1.5% Mn, while both the remanent magnetization M_r in zero field and the value M_{ex} obtained by extrapolation from high fields are a maximum for 3.1% Mn. The field dependence of $M(H)$ is linear beyond about $H = 3$ kOe, and the differential susceptibility dM/dH is essentially the same as the value for pure Cr at low temperatures.

Table 1. Parameters characterizing the field dependence of the magnetization $M(H)$ of alloys $Cr_{1-x}Mn_x$ and $(Cr + 1.3\%\ Si)_{1-x}Mn_x$ at temperature 5 K in the range -55 kOe $< H < 55$ kOe.

Alloy	Curve (figure 3)	H_c (Oe)	M_r (10^{-4} emu g^{-1})	M_{ex} (10^{-4} emu g^{-1})	dM/dH (10^{-6} emu g^{-1})
Cr +					
≪0.1% Mn	4	55	1.4	5	2.96
0.6	5	280	10	18	2.94
1.5	6	520	42	78	2.80
3.1	7	220	72	197	2.97
4.6	8	130	47	169	2.98
Cr + 1.3% Si +					
0.17% Mn	2	—	—	12	2.94
0.6	3	300	21	37	2.87

It is interesting to note on comparing curves 5 and 3 in figure 3 and table 1 that 0.6% Mn in Cr + 1.3% Si results in considerably larger values, by about a factor of two, of both M_r and M_{ex} than are obtained for CrMn samples containing the same amount of Mn. This result is presumably related to the increase in the amplitude of the SDW in the Si doped ternary alloy, which was found to be 1.07 μ_B in the commensurate phase of Cr + 1.37% Si [10] as compared with the low-temperature value of 0.43 μ_B for the incommensurate SDW in pure Cr.

Relaxation effects were not studied systematically, but the magnetization was found to relax from the ZFC state to the FC state when a field $H = 100$ Oe was applied, and conversely. Just as in the case of a conventional spin glass [8], the relaxation is much slower in the FC state than in the ZFC state and the magnetization changes as the logarithm of the elapsed time.

The model we propose to explain the spin-glass behaviour assumes the existence of a frozen moment M on a single Mn impurity atom in the Cr host. The moment of about 4 μ_B on the Mn atom responsible for the Curie–Weiss temperature dependence of $\chi(T)$ in the paramagnetic phase evidently freezes at the Néel transition, since in alloys containing up to about 4% Mn the susceptibility is only weakly dependent on temperature just as in pure Cr [5, 9]. We postulate that M is oriented along the same cube axis as the moment m of the Cr atom for which the Mn atom substitutes, or along the polarization direction of the SDW in the incommensurate SDW phase. The direction of M at higher temperatures may however be either parallel or antiparallel to m, the latter corresponding to a metastable configuration. The magnetic anisotropy will increase in magnitude as temperature decreases, and we suppose further that the energy of the antiparallel configuration increases faster than that of neighbouring orientations, so that at some temperature T_p this configuration becomes unstable. At this pinning temperature the directions of the Mn moments remain unchanged, but this phase of the SDW changes by $\tilde{a}$ so as to make $m \parallel M$, i.e., to make M antiparallel to the moments of its Cr neighbours.

Considering now the relative directions of M on two neighbouring Mn atoms, in some cases there will be frustration for Cr atoms on a surface between them, resulting from the competition between the two polarization directions of the SDW required for the moment of the Cr atom to be in phase with one or the other. When all the Mn atoms are thus considered, they will be seen to partition the SDW into phase domains that surround each Mn atom, or pair of atoms or more whose moments are in phase with each other, the different domains being separated by surfaces of frustration of the moments of the Cr atoms.

These frustrated Cr atoms are responsible for the increase in $\chi(T)$ below the pinning temperature, $T_p \sim 40$ K, in dilute $Cr_{1-x}Mn_x$ alloys. As x increases, however, the number of pairs, triplets, and higher-order clusters will grow at the expense of the single Mn atoms, and the frustration surfaces will eventually disappear. Thus with random distribution only 25% of the Mn atoms will be single in the case $x = 16\%$, and indeed the sharp increase in $\chi(T)$ at $T_p \sim 40$ K ceases at about this composition [6].

It is important to emphasize that this mechanism for frustration is independent of the concentration of Mn impurity. In principle, only two moments M_1 and M_2 in an otherwise perfect lattice would create a surface of frustrated Cr atoms, if the phase shift of the SDW at the pinning temperature were such as to destroy its coherence. The value of T_p is determined by the temperature dependence of the crystal fields responsible for the magnetic anisotropy, and not by the RKKY interaction between neighbours that depends on their separation as in a conventional spin glass such as CuMn.

Friedel and Hedman [12] postulated that the moment of the Fe atom in CrFe alloys in the dilute limit pins the phase of the incommensurate SDW. However the magnetization of

dilute CrFe alloys obeys a Curie–Weiss law in the magnetically ordered SDW phase as well as in the paramagnetic phase, which is attributed by Friedel and Hedman to the freedom of the Fe moment to rotate, thus locally distorting the phase of the SDW that is pinned to its orientation.

Aidun *et al* [11] analysed the temperature dependence of the magnetic susceptibility of $Cr_{1-x}Mn_x$ alloys with x ranging from 2 to 16% Mn and found that the Curie–Weiss law seen in the ordered phase in the higher-concentration alloys may be explained by assuming the moment on a single Mn atom to be frozen below the Néel transition, while the effective moment on a ferromagnetically coupled nearest-neighbour pair is about 4 μ_B.

The new type of spin glass seen in CrMn alloys differs fundamentally from a conventional spin glass in that moments on the antiferromagnetic host lattice become frustrated at a constant characteristic pinning temperature, whereas in the latter case the moments on the impurity atoms are frustrated until they freeze into a spin glass at a freezing temperature determined by their separation. The feature that the new spin glass has in common with the conventional system is frustration, which will lead to hysteretic behaviour in both cases.

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