Magnetic properties of Cr–Fe–Mn alloys

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A R T I C L E   I N F O
Article history:
Received 16 January 2008
Received in revised form 23 July 2008
Available online 31 July 2008

Keywords:
Cr alloy
Magnetization
Electrical resistivity
Magnetoresistivity
Specific heat
Thermal expansion

A B S T R A C T

The magnetic behaviour of a Cr 100−xFe 20Mnx alloy system with x = 2, 7, 10, 13 and 22 has been investigated in the temperature range 2–400 K through measurements of magnetization, electrical resistivity, magnetoresistivity, specific heat and thermal expansion. The temperature vs. Mn concentration magnetic phase diagram of the system is rich in magnetic behaviour with ferromagnetic (FM), antiferromagnetic (AFM) and paramagnetic phase regions and a spin-glass (SG) region at the lowest temperatures. Phase transition temperatures amongst these different magnetic phases could be identified from well-defined anomalies of magnetic origin that are displayed by graphs of the above-mentioned physical properties as a function of temperature. The time relaxation of the thermoremanent, isothermal remanent and field-cooled magnetizations below and above the SG freezing temperature show unusual aspects. These relaxations do not follow the usual superposition principle that is expected for typical SG materials. Negative giant magnetoresistance (GMR) is observed in the alloys at 4 K. The GMR initially increases sharply on increasing the Mn content in the alloy system, followed by a tendency towards a saturation negative value for concentrations of more than about 10 at% Mn. Low-temperature plots of C p / T vs. T 2, where C p is the specific heat, present anomalous behaviour for alloys with x = 2, 10 and 22. For x = 2 the plot shows an upturn at the lowest temperatures that changes over to a prominent downturn for x = 10 and 22. This behaviour is attributed to Fe concentration fluctuations in the alloys, confirming the theoretical model of Matthews.

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1. Introduction

The interest in the spin-density-wave (SDW) properties of Cr and its dilute alloys is well documented [1,2], and follows mainly from a very rich variety of magnetic phases and magnetic phase transitions that are introduced when Cr is alloyed with various elements of the periodic table. The case of the Cr 100−xFe x alloy system is of particular interest due to its unusual magnetic phase diagram in the temperature–concentration plane. This diagram exhibits separate paramagnetic (PM), longitudinal incommensurate (l) SDW antiferromagnetic (AFM), transverse ISDW AFM, commensurate (C) SDW AFM, ferromagnetic (FM) and spin-glass (SG) phase regions [2–5]. The PM–AFM phase line extends down T = 0 K at about 16 at% Fe, while between 16 and 19 at% Fe a SG phase appears at low temperatures and eventually a FM phase is established for concentrations x > 19 at% Fe [4].

Alloying Cr with Mn changes the magnetic state by increasing the electron concentration, bringing the electron and hole octahedral Fermi surface sheets closer in dimensions in reciprocal space, thereby moving the SDW Q-vector towards commensurability and increasing the Néel temperature (T N) [2]. The magnetic state of a Cr–Fe alloy can also be adjusted by replacing Cr systematically with Mn, keeping the Fe content fixed [6]. This results for instance in a crossing of the PM–AFM and PM–FM phase lines at a certain Mn concentration, x c, on the magnetic phase diagram of Cr 100−y−Fe yMnx alloy systems with a certain fixed value of y, e.g. x c ≈ 20 at% Mn for a Cr 75–Fe 25 Mn x alloy system [6]. Depending on x in such a ternary alloy, a PM–FM–SG phase transition sequence for x < x c, or a PM–AFM–FM–SG one for x > x c, can be traversed as a function of temperature [6].

The magnetic state at low temperatures in this type of alloy system is heterogeneous for x > x c, consisting of FM regions imbedded in an AFM matrix [7–8] that results in competing FM and AFM interactions [8]. As the temperature is decreased from the PM phase there appears a PM–AFM Néel phase transition into a magnetically heterogeneous phase in which parts of the alloy transform to an AFM phase, while the rest remains in the PM phase [8]. On further cooling, these PM regions gradually undergo a PM–FM phase transition and the system finally reaches a SG state at the lowest temperatures [8].
Giant magnetoresistance (GMR) behaviour is observed \([9,10]\) in the \(\text{Cr}_{100-x}\text{Fe}_x\) alloy system, reaching a maximum GMR value at \(x\) around 20 at\% Fe. Due to this, there is renewed interest in the \(\text{Cr}_{100-x}\text{Fe}_x\) alloy system, particularly in the influence of Mn or V addition on the GMR properties at temperatures where AFM and FM domains coexist \([7,8,11]\). Addition of one of these two elements strengthens or weakens, respectively, the SDW AFM interactions in \(\text{Cr}_{100-x}\text{Fe}_x\) \([2]\) and has a significant influence on the GMR. The role of competing AFM and FM interactions on the magnetic and GMR behaviour of \(\text{Cr–Fe–Mn}\) and \(\text{Cr–Fe–V}\) alloy systems are, however, not well understood at present \([7]\). In order to contribute in this regard we report here on the magnetization, electrical transport properties (including GMR), specific heat and thermal expansion of a \(\text{Cr}_{100-x}\text{Fe}_x\text{Mn}_y\) (nominal concentration) alloy system. This alloy system was chosen since, depending on the value of \(x\), it represents both the above-mentioned sequences of magnetic phase transitions and, furthermore, has a constant Fe content of \(\approx 20\text{ at}\%\) Fe for which the GMR in \(\text{Cr}_{100-x}\text{Fe}_x\) is at a maximum value.

2. Experimental methods

Two sets of \(\text{Cr}_{80-x}\text{Fe}_{20}\text{Mn}_x\) alloys were used in this study. One set of three alloys were prepared by arc-melting in a purified argon atmosphere from 99.996% pure Cr, 99.999% pure Fe and 99.99% pure Mn. The ingots were melted five times in succession, turning them upside-down between each melt, then crushed and re-melted, a process that was repeated twice to ensure homogeneity. Another set of two alloys were prepared by induction heating from electrolytic (99%) Cr, electrolytic (99%) Mn and industrial grade Fe (containing impurities: C, 0.14–0.22%; Mn, 0.3–0.65%; Si, \(< 0.3\%\); S, \(< 0.05\%\); P, \(< 0.045\%\)). These two alloys were included in this study in order to probe the effect of impurity deviations of the concentrations measured for each element at the different measuring points. The deviation is taken as an indication of the homogeneity of the alloy samples. Some Cr and, in particular, Mn was evidently lost during melting of the alloys. This is ascribed to the comparatively high vapour pressure of Cr in the molten state and to the fact that the boiling point of Mn is close to the melting point of Cr. Although we tried to compensate for Cr and Mn losses in the constituent weights before melting, the results of our elemental analyses prove that the desired 20 at\% Fe was consequently also difficult to pin down. The arc-melted samples are of quality in this regard nevertheless, with a maximum satisfactory deviation of less than 10% from the average Fe concentration.

From Table 1 the overall homogeneity appears markedly better for the arc-melted than for the induction-melted alloys, which is partly ascribed to the much better purity of the constituent materials in the arc-melted alloys compared to that of the induction-melted ones. The former group of alloys is referred to in this paper as the “arc-melted” alloys and the latter group as the “induction-melted” alloys. Only a limited study, for comparison purposes, is reported on the induction-melted alloys.

The results of powder XRD diffraction measurements on our samples (not shown) at room temperature reveal the alloys to be body-centred cubic and single phase.

All measurements, except for thermal expansion, were done using quantum design (QD) PPMS equipment; including the QD VSM option for magnetization, the QD adiabatic heat pulse calorimetric option for specific heat and QD four-probe DC-electrical resistivity option. Thermal expansion measurements were done relative to a \(\text{Cr}_{95}\text{V}_5\) alloy, which remains PM at all temperatures \([12]\), using standard strain gauge techniques.

Magnetization, \(M(T)\), measurements in a constant applied magnetic field were done in field cooling (FC) and zero-field cooling (ZFC) conditions in the temperature range 2–300 K. Thermoremanent magnetization (TRM) measurements were done by first cooling the alloy from room temperature down to 4 K in a constant applied magnetic field. The field was then kept constant at this temperature for a waiting time, \(t_w\), followed by measurements of the magnetization, \(M_{\text{TRM}}(t_{w0}, t_{\text{obs}})\), as a function of observation time, \(t_{\text{obs}}\), starting at the instant that the field is switched off after the waiting time has elapsed. The isothermal remanent magnetization (IRM) was measured by ZFC the sample from room temperature down to 4 K, and waiting at this temperature for a time \(t_w\) before a constant magnetic field was applied. The magnetization, \(M_{\text{IRM}}(t_w, t_{\text{obs}})\), was then measured in this constant field as a function of observation time. Relaxation of the field-cooled magnetization (FCM) was measured by cooling the sample from room temperature down to 4 K in a constant field, waiting for time \(t_w\) without changing the temperature or field, and then measure \(M_{\text{FC}}(t_w, t_{\text{obs}})\) as a function of observation time in the same field.

Magnetic hysteresis loops were recorded at temperatures of 2 and 60 K, chosen for reasons described below.

3. Results and discussion

3.1. Magnetization

Fig. 1(a) shows the FC and ZFC magnetization, \(M\), as a function of temperature for \(\text{Cr}_{77}\text{Fe}_{21}\text{Mn}_2\), \(\text{Cr}_{68}\text{Fe}_{22}\text{Mn}_{10}\) and \(\text{Cr}_{58}\text{Fe}_{20}\text{Mn}_{22}\).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Preparation method and purity of starting materials</th>
<th>Cr (at%)</th>
<th>Standard deviation</th>
<th>Fe (at%)</th>
<th>Standard deviation</th>
<th>Mn (at%)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}<em>{77}\text{Fe}</em>{21}\text{Mn}_2)</td>
<td>Arc-melted ((&gt;99.99%))</td>
<td>77.2</td>
<td>(\pm 0.5)</td>
<td>20.9</td>
<td>(\pm 0.5)</td>
<td>2.0</td>
<td>(\pm 0.3)</td>
</tr>
<tr>
<td>(\text{Cr}<em>{77}\text{Fe}</em>{21}\text{Mn}_2)</td>
<td>Induction-melted ((&gt;99%))</td>
<td>70.7</td>
<td>(\pm 1.1)</td>
<td>22.0</td>
<td>(\pm 3.2)</td>
<td>7.3</td>
<td>(\pm 2.8)</td>
</tr>
<tr>
<td>(\text{Cr}<em>{68}\text{Fe}</em>{22}\text{Mn}_{10})</td>
<td>Arc-melted ((&gt;99.99%))</td>
<td>67.9</td>
<td>(\pm 0.5)</td>
<td>21.7</td>
<td>(\pm 0.4)</td>
<td>10.4</td>
<td>(\pm 0.3)</td>
</tr>
<tr>
<td>(\text{Cr}<em>{68}\text{Fe}</em>{22}\text{Mn}_{10})</td>
<td>Induction-melted ((&gt;99%))</td>
<td>64.2</td>
<td>(\pm 2.1)</td>
<td>23.4</td>
<td>(\pm 2.9)</td>
<td>12.4</td>
<td>(\pm 4.5)</td>
</tr>
<tr>
<td>(\text{Cr}<em>{58}\text{Fe}</em>{20}\text{Mn}_{22})</td>
<td>Arc-melted ((&gt;99.99%))</td>
<td>58.2</td>
<td>(\pm 0.8)</td>
<td>20.0</td>
<td>(\pm 0.4)</td>
<td>21.8</td>
<td>(\pm 0.6)</td>
</tr>
</tbody>
</table>

The standard deviation reflects the variation of the alloy content amongst the analyses at the different points. The purities of the starting materials used are given in brackets (second column). The alloys are grouped in order of increasing Mn content.