MAGNETIC PROPERTIES OF MnPt AND CoPt

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ABSTRACT

Magnetization measurements were conducted on ordered and disordered polycrystalline specimens of MnPt and three Co-Pt alloys between 4.2 and 293°K. The magnetic data, while confirming the onset of antiferromagnetism in the ordered MnPt, reveal the presence of ferromagnetic regions in the disordered MnPt. Chemical order tends to exert a pronounced (~30%) adverse effect on saturation magnetization ($M_{s,0}$) of the Co-Pt alloys at 0°K near the equiatomic composition. Meanwhile, the effect of Co concentration on $M_{s,0}$ of the Co-Pt alloys is shown to be appreciable only when the Co content exceeds 50%.

INTRODUCTION

Platinum and transition metals of the iron group form a series of isomorphous solid solutions at the equiatomic composition. In the disordered state, five NPt alloys, namely, CrPt, MnPt, FePt, CoPt, and NiPt crystallize into the face-centered cubic lattice. All these alloys tend to order chemically into the $L1_0$ - or CuAu I-type superlattice, of which the c/a ratio is <1 based on the face-centered tetragonal structure, with room temperature values ranging from 0.915 for MnPt¹ to 0.969 for CoPt².

Investigation of the magnetic behavior of the NPt alloys was initiated by Kussmann³ in 1935. Shortly thereafter⁴, the ferromagnetic CoPt was found to display exceptionally high values of coercive force and $(BH)_{max}$, thus making the alloy an attractive permanent magnet. Besides the commercial potential of CoPt, interest in the NPt alloys lies in the prospect that, because of the striking resemblance in their crystal structure and their tendency to ordering, the alloys constitute a system within which the variation of magnetic properties with the species of magnetic component N and with the state of order could shed light on the distribution and interaction of magnetic moments in transition-metal alloys.

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Data for the disordered MnPt disclose a nonlinear M-H relationship in the same temperature range. Shown in Fig. 1 is a typical curve for the disordered MnPt at 4.2°K, of which the slope is positive, but decreasing progressively. The latter plot seems to imply the presence of ferromagnetic regions, possibly in the sense of micromagnetism. To test this implication, we first measured M of the disordered MnPt between $+H_{\max}$ and $-H_{\max}$ at 4.2 and 293°K. A resolvable hysteresis loop emerged at both temperatures. The 4.2° loop is shown by the solid curves in Fig. 2. To see whether the emergence of this hysteresis loop is related to an unidirectional anisotropy induced by the exchange interaction between ferromagnetic and antiferromagnetic regions⁸, we further cooled the specimen from room temperature to 4.2°K in a magnetic field of 20 koe. The hysteresis loop subsequently measured parallel to this field is shown by the dashed curves in Fig. 2. The magnetic cooling has neither introduced asymmetry with respect to the origin nor changed the main features (e.g., the coercive force and remanence) of the loop; it only opened up the loop toward the tips and slightly raised the maximum value of M at $H_{\max}$. The results showing the insignificant effect of the magnetic cooling on the hysteresis loop suggest that the present case differs from that seen in the disordered Ni_3Mn ⁹, for which exchange anisotropy plays a vital role in the hysteresis behavior.

According to neutron diffraction data⁶ for the ordered MnPt, only Mn atoms carry magnetic moments of $4.3 \pm 0.2 \mu_B$, which are aligned antiferromagnetically in alternate (010) planes in the c-axis. Thus in terms of the Heisenberg theory, a negative exchange integral J exists between atom pairs of Mn in the nearest neighbors (NN) and a positive, but smaller, J exists between Mn-Mn pairs in the next nearest neighbors. Since the number of NN pairs of Mn is increased from 4 to 6 and the distance is decreased from 2.831 Å to 2.749 Å on going from the ordered to the disordered state, ferromagnetism is not expected in the disordered MnPt. The present results probably imply a nonuniform distribution of the constituent atoms, leading to a division of the crystals into regions, some rich in Co and others rich in Pt. The Pt-rich regions having compositions corresponding to 63-83 at % Pt-Mn give rise to the magnetic behavior shown in Figs. 1 and 2 because the latter alloys are known to be ferromagnetic.⁶

Despite the initial work by Kussmann and more recent studies by Pearson et al.⁵ and by Krén et al.⁶, magnetic data for the NPt alloys were still incomplete. For instance, new susceptibility data⁷ for NiPt detected a change in the mode of spin coupling from ferromagnetic to antiferromagnetic as a result of the disorder→order transition. The latter result has motivated us to examine certain aspects of the magnetic behavior of MnPt and CoPt. The present report will reveal (1) the presence of ferromagnetic regions in the disordered MnPt, (2) a pronounced adverse effect of chemical order on the extrapolated value of saturation magnetization to 0°K ($M_{s,0}$) of CoPt, and (3) highly irregular variations of $M_{s,0}$ with Co concentration of the Co-Pt alloys near the equiatomic composition.

EXPERIMENTAL PROCEDURE

Four alloys (MnPt, $\text{Co}_{0.54}\text{Pt}_{0.46}$, CoPt, and $\text{Co}_{0.46}\text{Pt}_{0.54}$) were prepared from high purity (>99.98%) metals by arc melting. To attain composition homogeneity, the ingots were remelted several times on alternate sides and homogenized at appropriate temperatures for 12-46 hrs in an atmosphere of purified helium gas. Magnetic specimens were prepared in short cylinder form by machining. Disordered specimens were obtained by quenching into brine from 1125 and 950°C, respectively, for MnPt and Co-Pt alloys. Ordered specimens were obtained by prolonged annealing at several temperatures below the order-disorder transition temperature. A vibrating sample magnetometer equipped with a liquid helium metal dewar was used to measure magnetization under a field of maximum strength of 20 koe.

RESULTS AND DISCUSSION

(I) Kind of Magnetism in MnPt Below 293°K

Magnetic data obtained for the ordered MnPt between 4.2 and 293°K yield a linear relationship between magnetization (M) and magnetizing field (H). A typical linear M-H plot at 4.2°K is shown in Fig. 1. The deduced values for magnetic susceptibility (χ) show a slight, nonlinear decreasing tendency with decreasing temperature in the χ versus T plot. These results are consistent with the onset of antiferromagnetism established in the ordered MnPt by previous workers^{5,6}.

(II) The Effect of Chemical Order and Co Concentration on M_s of CoPt and Related Alloys

Although the ferromagnetic CoPt alloy attracted numerous studies in the 1950's¹⁰, interests had been focused on structure-sensitive magnetic properties. In a more recent study, McCurrie and Gaunt¹¹ observed an 18% decrease in M_s of $\text{Co}_{0.48}\text{Pt}_{0.52}$ at 77°K as a result of chemical order. To further evaluate the effect of chemical order and Co content on M_s , we obtained the $M_{s,0}$ values at 0°K for CoPt and two related alloys by extrapolation first in the M vs $1/H$ plot and then in M_s vs T plot. The extrapolated values for the three alloys in both states of order are listed in Table 1. A persistent, 29-35% decrease is seen of $M_{s,0}$ in all three alloys upon ordering. Our data also reveal that the variations in $M_{s,0}$ of CoPt caused by a 4% change in Co content are larger on the Co-rich side than those on the Pt-rich side in both states of order.

The observed effect of chemical order and Co content on $M_{s,0}$ can be related to the crystal and magnetic structures. X-ray data for CoPt² gave $a=3.751$ Å in the disordered phase and $a=3.793$ Å and $c=3.675$ Å in the $L1_0$ superlattice at room temperature. From neutron data, van Lear¹² detected a total moment of 1.90 ± 0.01 μ_B per formula CoPt. (Our $M_{s,0}$ values for CoPt give 2.12 and 1.43 μ_B per formula in the disordered and ordered states, respectively, indicating that van Lear's sample was only partially ordered.) The total moment was seen to split into ≈ 1.6 and ≈ 0.3 μ_B for the Co and Pt atom, respectively. In the disordered state, each atom is surrounded, on the average, by 6 Co and 6 Pt atoms at the same distance of $d_{NN}=2.653$ Å; whereas in the superlattice, each Co(or Pt) atom is surrounded by 8 Pt(or Co) atoms at $d_{NN_1}=2.649$ Å and by 4 Co(or Pt) atoms at $d_{NN_2}=2.683$ Å. In view of these environmental changes, we interpret our experimental results as implying that ordering causes a decrease in the moment of Co atoms that is considerably more than the possible increase in the moment induced at the Pt sites. The observed irregular effect of Co content on $M_{s,0}$ may be explained similarly in terms of changes in the number of Co-Co and Co-Pt pairs in the nearest neighbors.

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Table 1. Extrapolated Values of Saturation Magnetization to 0°K for Three Co-Pt Alloys.

$\text{Co}_{0.54}\text{Pt}_{0.46}$		CoPt		$\text{Co}_{0.46}\text{Pt}_{0.54}$	
Disord.	Order.	Disord.	Order.	Disord.	Order.
$M_{s,0}$, emu/g:					
53.5	37.8	46.6	32.1	45.0	29.3
(A) Change in $M_{s,0}$ caused by ordering					
15.7(29%)		14.5(31%)		15.7(35%)	
(B) Change in $M_{s,0}$ caused by variation in % Co;disord.					
6.9(15%)		1.6(3.4%)			
(C) Change in $M_{s,0}$ caused by variation in % Co;ordered					
5.7(18%)		2.8(9%)

Fig. 1. Field dependence of magnetization in the disordered and ordered MnPt at 4.2°K.

Fig. 2. Hysteresis loop displayed by the disordered MnPt at 4.2°K after cooling from room temperature in zero field (solid curves) and in a field of 20 koe (dashed curves).