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Effect of atomic order on some physical properties of $\text{Co}_{25}\text{Pt}_{75}$

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Abstract

$\text{Co}_{25}\text{Pt}_{75}$ alloy was made by the induction melting method. In order to achieve various degrees of atomic order in the sample, annealing and quenching techniques were employed. We are interested in studying how atomic order would affect the physical properties of CoPt_3 , such as its lattice constant, thermal expansion coefficient, specific heat, and electrical resistivity. It is found that, on ordering in CoPt_3 , the f.c.c. lattice expands isotropically. Correspondingly, the sample length shrinks when temperature is raised above the order-disorder transition temperature T_x . Both the high temperature resistivity and the specific heat data indicate that the CoPt_3 system does not have a gap-type behaviour. Around T_x , as well as the long-range order, there may exist a short-range order in CoPt_3 , as implied from the resistivity measurement.

Keywords: Atomic order; Physical properties; Annealing; Quenching techniques

1. Introduction

According to the phase diagram for Co–Pt alloys [1], there are two atomic order-disorder transformation regions, namely the allotropic CoPt and CoPt_3 . The ordered phase of CoPt below 1098 K has the face-centred tetragonal (f.c.t.) structure of CuAu (L1_0) type, and that of CoPt_3 below 1023 K has the f.c.c. structure of Cu_3Au (L1_2) type.

Because of the lattice distortion (from f.c.c. to f.c.t.) on ordering in CoPt , it has been known that some physical properties are also changed accordingly. For example, (1) near the order-disorder transformation temperature ($T_x \approx 1098$ K) electrical resistivity $\rho(T)$ decreases as the alloy becomes disordered [2,3], and (2) the electronic specific heat coefficient γ of disordered CoPt is larger than that of ordered CoPt [4]. These facts strongly suggest that because of atomic ordering in CoPt a superlattice wavevector \mathbf{Q} connects two points of the same sheet of the Fermi surface, $\mathbf{Q} = 2\mathbf{k}_F$, where \mathbf{k}_F is the Fermi wavevector. As a result, new Brillouin zones are formed, and near them energy gaps open up. Detailed explanations have been given in Refs. [2] and [3].

Compared with CoPt , CoPt_3 is a system which has not been thoroughly studied for the atomic order effect. In this paper, we shall focus on the following physical properties of CoPt_3 in order to discuss their

changes related to the degree of atomic order: lattice constant, electrical resistivity, specific heat, and thermal expansion coefficient.

2. Experiments

Stoichiometric $\text{Co}_{25}\text{Pt}_{75}$ alloy was made in an induction furnace. In order to achieve the various degrees of order in the sample, it was annealed at T_Q for a time period Δt and then quenched in salt water. For the highest degree of order, $T_Q = 868$ K, $\Delta t = 48$ h, and furnace cooling was used. An X-ray diffractometer made by Rigaku was employed, using the $\text{Cu K}\alpha$ wavelength, to analyse the phase structure and the lattice constant in the sample.

For the high temperature resistivity measurement, the sample was placed in a quartz tube, pumped to 10^{-3} Torr. In the vicinity of the sample, a type K thermocouple was attached for temperature readings. The heating rate of the furnace was about $2-3\text{ K min}^{-1}$. An alternating current and four-probe method were used to measure the resistivity. For the residual resistivity measurement, the sample is simply immersed in a liquid helium bath to maintain a constant temperature of 4 K. Here, we use the symbol $\rho_0 = \rho_0(T_Q, T = 4\text{ K})$ to indicate the residual resistivity of the CoPt_3 sample quenched from T_Q .

After a sufficiently long time for equilibrium to be reached at T_Q , the quenching rate is supposed to be fast enough that the atomic disorder at T_Q is frozen in the sample. It is known that in CoPt_3 alloy the ordering equilibrium occurs through a relaxation process. The relaxation time obeys an Arrhenius law

$$\tau = \tau_0 \exp(E_A/k_B T) \quad (1)$$

where τ_0 is a constant, k_B is the Boltzmann constant, and E_A is the activation energy. For CoPt_3 , $\tau_0 = 1 \times 10^{-14}$ s and $E_A = 3.12$ eV [5]. Then, a simple calculation shows that when $T_Q \approx 870$ K, $\tau \approx 166$ min, and when $T_Q \approx 1073$ K, $\tau \approx 4.3$ s. Usually, in order to assume safely the equilibrium of the entire sample, the minimum annealing time is set at least as 10τ . Then, it is considered that CoPt_3 has a rather slow ordering kinetics. However, our anneal and quench operations all followed the estimations given above.

The high temperature thermal expansion data were obtained from a TMA7 thermal mechanical analyser made by Perkin-Elmer. The length of the sample could be continuously monitored as a function of furnace temperature. The heating rate was 3 K min^{-1} .

As to the low temperature (1-4 K) specific heat measurement, the d.c. relaxation method was used. The details are described elsewhere [4]. At low temperatures, specific heat C_p data can be fitted by equation

$$C_p/T = \gamma + AT^2 \quad (2)$$

Our goal is to find how γ is affected by the atomic orderliness in the sample. Hence, we measured γ , when the sample was disordered ($T_Q = 1073$ K), and measured it again, when the sample was quasi-ordered (annealed at 868 K for 48 h and furnace cooled).

3. Results and discussion

Table 1 summarizes the lattice constant data of CoPt_3 after different thermal treatments. By quenching from $T_Q = 1073$ K, we obtain single f.c.c. disor-

Table 1
The effect of atomic order on the lattice constant a of CoPt_3

	a_0 (Å)	a_d (Å)
$T_Q = 1073 \text{ K}, \Delta t = 1 \text{ min}$	—	3.854
$T_Q = 963 \text{ K}, \Delta t = 5 \text{ h}$	3.891	3.852
$T_Q = 868 \text{ K}, \Delta t = 48 \text{ h}$	3.899	3.855

T_Q is the quenching temperature and Δt is the annealing time. a_0 is the lattice constant of ordered phase and a_d is that of disordered phase.

dered phase in CoPt_3 , and the lattice constant $a_d = 3.854$ Å. If T_Q is lower than 1073 K (the order-disorder transition temperature T_x) and the annealing time is prolonged, we find (1) for $T_Q = 963$ K ($\Delta t = 5$ h) that the ordered and disordered phases coexist in the sample. Furthermore, the diffraction lines for the ordered phase become split, and (2) for $T_Q = 868$ K ($\Delta t = 48$ h) the split lines of the ordered phase merge together. Although under this annealing condition there is still a minor disordered phase in the sample, the diffraction line intensity of the ordered phase becomes much stronger, as T_Q is lowered from 963 K to 868 K. The lattice constant a_0 of ordered phase is determined to be 3.899 Å.

From the X-ray data it is concluded that (1) the order-disorder transformation occurs heterogeneously with a two-phase field [6], (2) $a_0 > a_d$ indicates the opposite tendency from the lattice change of an ordinary order-disorder transformation, and (3) the complete single ordered phase may show up only after a very long-time anneal. It is interesting to compare our a_0 and a_d data with those from Geisler and Martin [7]; they also found a_0 to be slightly larger than a_d . However, the difference between a_0 and a_d in our sample is much larger.

A thermal expansion test was done on the quasi-ordered CoPt_3 sample (which had been annealed at $T = 868$ K for 48 h). The result is shown in Fig. 1. Near the order-disorder transition temperature T_x , an inward kink of the ΔL curve is found. This means that there is a lattice contraction in CoPt_3 due to the change in atomic order, which overcomes the effect of thermal expansion on anharmonic terms. Thus, it is confirmed that for CoPt_3 a_0 is larger than a_d .

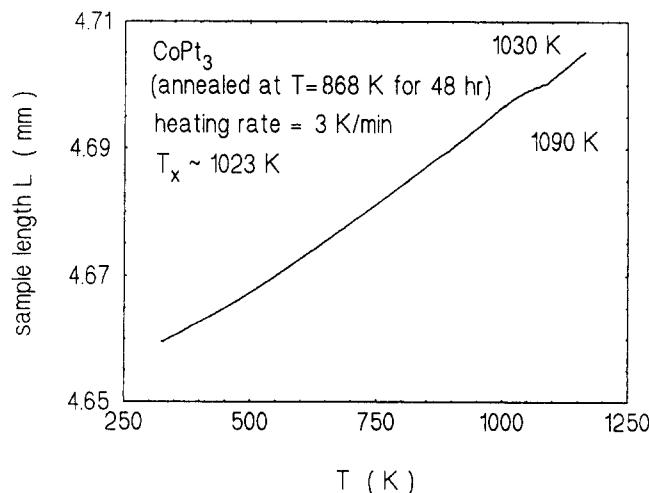


Fig. 1. The change in sample length L of a quasi-ordered CoPt_3 sample from $T = 300$ to 1200 K. T_x is the order-disorder transition temperature.

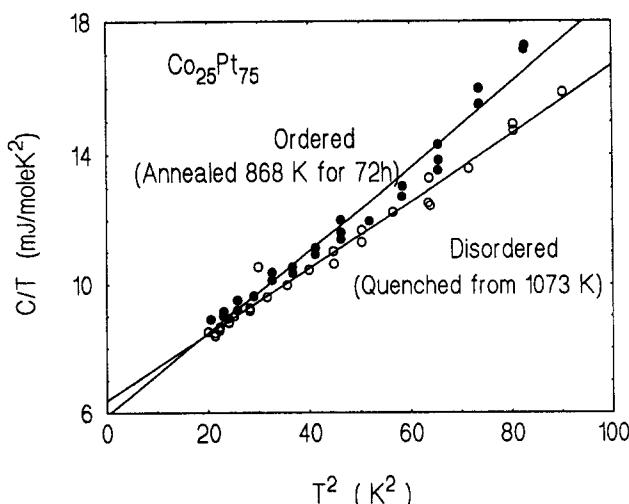


Fig. 2. The specific heat data of disordered and ordered CoPt_3 are plotted to fit the equation $C/T = \gamma + AT^2$, where γ is the electronic specific heat coefficient and A is related to the Debye temperature.

As to the comparison of γ between ordered and disordered CoPt_3 , the corresponding fitting of Eq. (2) for each case is illustrated in Fig. 2. Then, we discover that γ_d (disordered) = $6.25 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which is slightly higher than γ_o (ordered) = $5.95 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Although there is a difference between γ_d and γ_o , it is considered to be very small, and may be within the experimental errors of our low temperature calorimeter. Then, we conclude that the atomic ordering does not affect γ of CoPt_3 as against the case for CoPt . The Debye temperature θ_D of disordered CoPt_3 is estimated to be 265 K, and that of ordered CoPt_3 is 248 K. Here, it is understood that although both ordered and disordered CoPt_3 are ferromagnetic, the specific heat term due to magnons is rather minor, and can be safely neglected.

Fig. 3 shows the resistivity of quasi-ordered CoPt_3 from 300 to 1200 K. The whole $\rho(T)$ curve increases smoothly as the temperature is raised. There is no apparent discontinuous change in $d\rho/dT$ around either the Curie temperature T_c or the order-disorder transformation temperature T_x . In the former case, since $T_c \approx 773 \text{ K}$, the ordered and disordered phases may coexist as mentioned before, and Ref. [8] has also demonstrated a similar smearing effect in the magnetic susceptibility curve near T_c . In the latter case, it is obvious that $\rho(T)$ of CoPt_3 near T_x does not exhibit a gap-type behaviour. This conclusion is also in agreement with our previous conclusion drawn from the specific heat measurement. Hence, it leads us to speculate that (1) the 2% c axis contraction in CoPt on ordering may be crucial in defining the vector \mathbf{Q} and fulfilling the criterion $\mathbf{Q} = 2\mathbf{k}_F$, and (2) since all the conditions have been met for the ordered CoPt ,

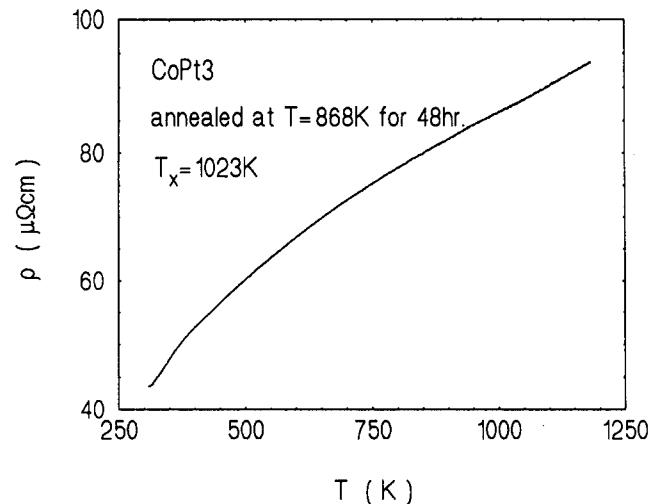


Fig. 3. The high temperature resistivity $\rho(T)$ plotted as a function of temperature from 300 to 1200 K. Initially, the sample was put in an ordered state by annealing it at $T = 868 \text{ K}$ for 48 h.

the Brillouin zone for the ordered CoPt_3 would be certainly too small to nest the Fermi surface again, assuming k_F of CoPt roughly agrees with that of CoPt_3 .

The residual resistivity of CoPt_3 samples quenched from various T_Q was also studied (Fig. 4). From the highest $T_Q = 1150 \text{ K}$ to the lowest $T_Q = 870 \text{ K}$, the residual resistivity ρ_0 drops by $9 \mu\Omega \text{ cm}$. Below $T_Q = 870 \text{ K}$, ρ_0 may reach a steady value, about $10 \mu\Omega \text{ cm}$. However, it is interesting to note that, even above $T_x = 1023 \text{ K}$, ρ_0 continues to increase, and it does not seem to approach a fixed value until T is higher than

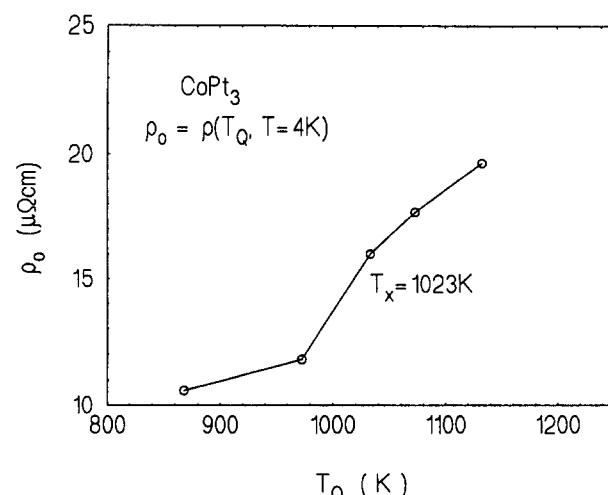


Fig. 4. The residual resistivity ρ_0 at 4 K of CoPt_3 samples quenched from various temperatures T_Q .

1200 K. This may indicate that, in addition to the long-range order effect on ρ_0 , there is probably a short-range order effect, which persists well above T_x . Here, we also conclude that the atomic ordering in CoPt_3 will lower the electrical resistivity, which is the normal-type behaviour as in contrast to the gap-type behaviour found in CoPt.

4. Conclusion

We have varied the degree of atomic order in CoPt_3 by quenching samples from various temperatures T_Q . The effect of atomic order on lattice constant, thermal expansion, specific heat, and electrical resistivity has been examined. It is found that when CoPt_3 undergoes a transition from the disordered to the ordered phase, the lattice is still f.c.c., but the lattice constant increases by 1.1%. From both the high temperature resistivity and the low temperature specific heat data, we discover that an energy gap does not exist for the CoPt_3 system. The electrical resistivity decreases monotonically as the sample becomes more ordered. The density of states at the Fermi level, as implied by γ , is not affected by the atomic order either.

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