Competitive contributions of short-range magnetic order and chemical disorder to the resistivity in $Co_{30}Pt_{70}$

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Abstract. A comparative study of the dependence on T of the resistivity in non-magnetic $Ni_{30}Pt_{70}$ and paramagnetic $Co_{30}Pt_{70}$ alloys in their ordered ($L1_2$-type structure) and disordered (A_1) phase is presented. In order to make measurements for as far as possible real thermodynamic equilibrium states, the heating rates were chosen taking into account previous ($Co_{30}Pt_{70}$) or present ($Ni_{30}Pt_{70}$) order kinetics data. We find that in $Ni_{30}Pt_{70}$ the resistivity can be analysed in terms of two main contributions: (i) a term of 4 K residual resistivity associated with the chemical disorder, and its variation with T, which is separately measured using a specific device; and (ii) a phonon-like term, proportional to T. In $Co_{30}Pt_{70}$, a further term associated with the spin-disorder scattering is present. In the paramagnetic range, this term decreases with T as the chemical disorder increases, the decrease being especially large at the order–disorder ($L1_2$–A_1) transition. Such behaviour is attributed to the existence of short-range magnetic order in the paramagnetic state of $Co_{30}Pt_{70}$, which would be enhanced by the increase of the chemical disorder, i.e. by the increase of the Co–Co coordination, thus reducing the spin-disorder contribution to the resistivity. All the data are in very good agreement with a previous comparative study of equi-atomic NiPt and CoPt phases, which led to a similar conclusion.

1. Introduction

In a previous paper, hereafter referred to as I (Leroux *et al* 1988), we demonstrated the existence of a large spin-disorder scattering term in the resistivity of the paramagnetic CoPt phase, whose amplitude gradually decreased as the chemical disorder increased. Such behaviour was attributed to the presence of short-range magnetic correlations (magnetic short-range order, MSRO) that were enhanced by the increase in Co–Co nearest-neighbour correlation when the chemical disorder increased, thus reducing the contribution of the spin-disorder scattering to the resistivity. This result is expected to be a general one in systems that display (i) 'good' magnetic moments (i.e. fairly localised) in their paramagnetic states (as most of Co- or Fe-based alloys do); (ii) order–disorder transitions in their paramagnetic states; and (iii) small changes in their electronic conduction states and in their Fermi surface shape on passing through the phase transformation (Rossiter 1979, 1980). This could apply for the $Co_{30}Pt_{70}$ phase which is ferromagnetic up to 390 K and in an ordered state of structure $L1_2$ up to about 1000 K, when $Ni_{30}Pt_{70}$, having the same $L1_2$ structure below about 800 K, is not magnetic in its

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disordered state (Besnus and Herr 1972, Beille *et al* 1974) and '*a fortiori*' in its ordered state (Dahmani *et al* 1985b). Thus, a comparative investigation of their resistivities, similar to that carried out for equi-atomic CoPt and NiPt phases, is possible.

The experimental procedure is briefly described in § 2. In order to ensure that we are measuring the resistivity of well defined thermodynamic states, we need knowledge of the order kinetics. Section 3 is devoted to recalling previous kinetics data for $Co_{30}Pt_{70}$ (Cadeville *et al* 1987) and to the results of a first kinetics study of $Ni_{30}Pt_{70}$. In § 4, resistivity data are presented, analysed and discussed. Section 5 gives the conclusions.

2. Methodology and experimental procedure

We chose to investigate the composition $M_{30}Pt_{70}$ (M = Ni and Co) instead of the stoichiometric one (MPt$_3$) because previous studies of the Co–Pt phase diagram (Dahmani 1985, Leroux *et al* 1988, Sanchez *et al* 1988) have shown that this composition is very close to that of the congruent point on the platinum-rich side. The related advantages are a narrow coexistence region of $L1_2$ and A_1 phases, and an order–disorder (O–D) transformation temperature (T_{O-D}) slightly higher than in CoPt$_3$, two conditions that favour the crossing of the O–D transformation region in conditions closer to the thermodynamic equilibrium. The exact details of the Pt-rich side of the Ni–Pt phase diagram are not well known. According to Dahmani *et al* (1985b) and Inden (1987), the $L1_2$ phase limit for $Ni_{30}Pt_{70}$ would be somewhat lower than 800 K.

A disadvantage of studying non-stoichiometric phases is that the resistivity difference between ordered and disordered states becomes small (see figure 6 of I), as a consequence of which the resistivity (residual or not) is much less sensitive to the degree of chemical long-range order (LRO) than in stoichiometric compounds.

The disordered and ordered alloys were prepared using the procedures described in I. For $Co_{30}Pt_{70}$, the ordering treatment makes use of the previous determination of the atomic relaxation times (Cadeville *et al* 1987). For $Ni_{30}Pt_{70}$, the following tentative ordering treatment was used: a quench from 923 K, followed by a series of anneals: 20 days at 773 K, 18 days at 756 K, 6 days at 743 K, 20 days at 733 K and, finally, an iced-water quench. At the end of this thermal treatment x-ray diffraction patterns were obtained so that we could observe the superstructure reflections of the $L1_2$ phase.

Resistivity measurements were made on samples rolled into strips a few centimetres long, 1 mm wide and about 50 μm thick. The strips were then subjected to ordering anneals. The microstructure of a $Co_{30}Pt_{70}$ sample, studied by TEM (Leroux 1989) reveals large ordered anti-phase domains of side 10 to 50 μm.

Two kinds of measurement were performed on each alloy: (i) *in situ* high-temperature measurements that yield the total resistivity ($\rho(T)$); and (ii) 4 K measurements with varying anneal temperature (T_A) on samples rapidly cooled from T_A that yield the contribution of the frozen-in chemical disorder ($\rho_0(T)$). The apparatus used for 4 K and *in situ* resistometry was as described in I.

3. Ordering kinetics

In order to arrive at equilibrium resistivity–temperature curves, it is necessary to make an appropriate choice of the heating rate for the *in situ* measurements and the annealing
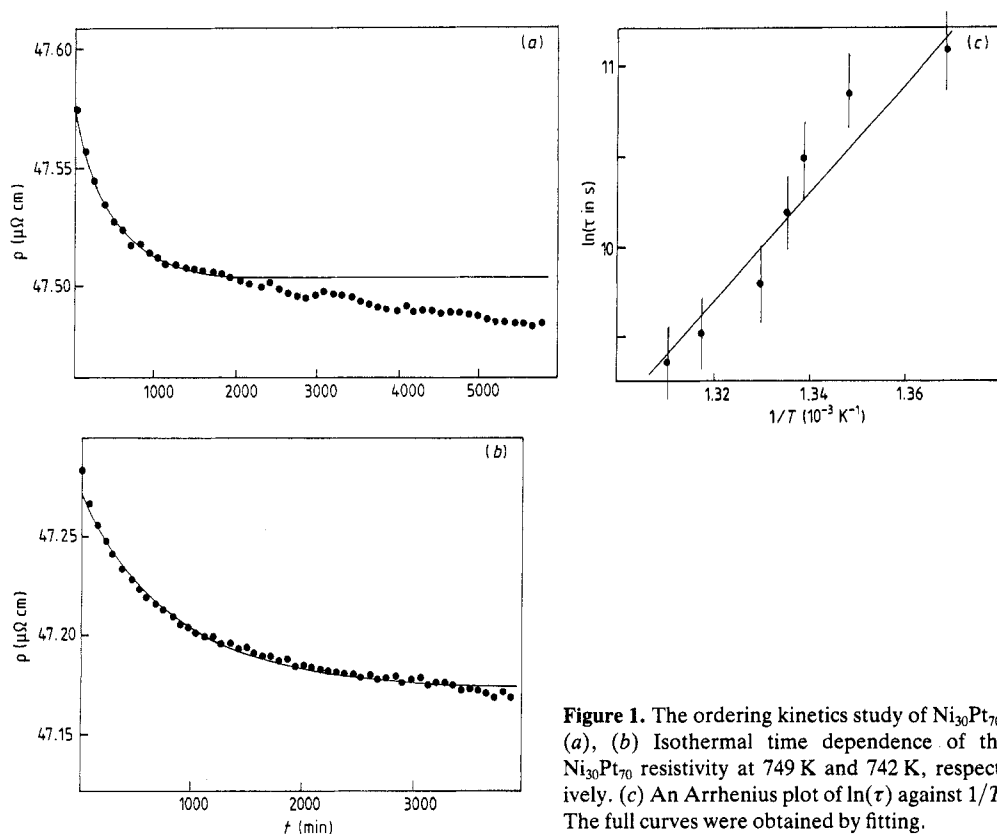
Figure 1. The ordering kinetics study of Ni$_{30}$Pt$_{70}$. (*a*), (*b*) Isothermal time dependence of the Ni$_{30}$Pt$_{70}$ resistivity at 749 K and 742 K, respectively. (*c*) An Arrhenius plot of ln(τ) against $1/T$. The full curves were obtained by fitting.

time for the 4 K resistometry. The study of the isothermal ordering kinetics was specifically aimed at yielding the desired information. Previous investigations (Dahmani *et al* 1985a) have shown that in ordered phases, for small departures from the equilibrium state, the resistivity increment or decrement associated with small changes of the LRO parameter (η) relaxes towards its equilibrium value according to a simple time-dependent exponential process (first-order kinetics) whose relaxation time τ varies with the temperature following an Arrhenius law ($\tau = \tau_0 \exp E_A/kT$). The constants τ_0 and E_A previously determined for Co$_{30}$Pt$_{70}$ are $\tau_0 = 4 \times 10^{-17}$ s and $E_A = 3.28$ eV (Cadeville *et al* 1987).

To get the corresponding information for Ni$_{30}$Pt$_{70}$, the following experiments were carried out. The measurements of the resistivity relaxations were performed at constant temperatures controlled within 0.5 K. After being mounted in the high-temperature resistometry device, the previously disordered sample was heated up to 793 K and rapidly cooled down to 719 K. This was done in order to quench in the vacancies that would otherwise control the *in situ* ordering at 719 K. This process initially caused an exponential-like decrease of the resistivity which, however, was followed by a quasilinear 'tail', still registering after five days. This was apparently an effect of an overlap of the increase of the degree of LRO and the ordered domain growth. In order to accelerate the latter, the sample was heated up to 759 K where a plateau of $R(T)$ was attained after about 15 h. Nevertheless, after subsequent re-cooling of the alloy down to 749 K the 'linear tail' of the resistivity relaxation was again present (figure 1(*a*)). The

Table 1. Relaxation times obtained for $Ni_{30}Pt_{70}$.

T (K)	731	742	747	749	752	759	763
τ (s)	65 460	52 320	36 120	26 580	17 880	13 500	11 520

Table 2.

	ρ_{4K} ($\mu\Omega$ cm) (disordered state)	ρ_{4K} ($\mu\Omega$ cm) (ordered state)	$\Delta^{D-O}\rho_{4K}$ ($\mu\Omega$ cm)
$Ni_{30}Pt_{70}$	21 ± 1	19 ± 1	2 ± 2
$Co_{30}Pt_{70}$	33 ± 1	14 ± 1	19 ± 2

kinetics curves were free of this effect (figure 1(b)) only after a re-annealing of the sample for 70 h at 771 K.

Finally, the resulting series of the isotherms registered between 730 and 763 K was analysed via a fitting of the function

$$R(t) - R(0) = (R(\infty) - R(0))(1 - \exp(-t/\tau)). \tag{1}$$

In the case where the curves show the 'linear tail', function (1) was fitted only to the initial points corresponding to the exponential-like resistivity relaxation (figure 1).

The relaxation times evaluated related to particular temperatures are displayed in table 1, while figure 1(c) shows an Arrhenius plot of these relaxation times, which indicates that the ordering activation energy ≈ 2.6 eV and $\tau_0 \approx 4 \times 10^{-14}$ s.

This leads us to draw two conclusions:

(i) in the case of the alloy $Ni_{30}Pt_{70}$ the temperature interval where the ordering kinetics is measurable—i.e. the process shows a reasonable rate—covers only a narrow region in the vicinity of T_{O-D} and thus the effect of ordered domain growth strongly influences the measurements;

(ii) the values of the estimated relaxation times (table 1) indicate that an accurate measurement of $\rho(T)$ would take weeks and be technically difficult to complete.

On the basis of the ordering kinetics data for the two alloys and taking into consideration the requirement of producing the resistivity curves within a reasonable time interval, we chose for the *in situ* measurements a heating rate of 5 K h^{-1} in the region of interest. Under these conditions, the resistivity curves correspond to equilibrium states for temperatures above 850 K in $Co_{30}Pt_{70}$, i.e. well below T_{O-D}, and above 800 K in $Ni_{30}Pt_{70}$, i.e. just above T_{O-D}. Moreover, in order to shorten the measurement time yet more, the low-T parts of the curves were obtained using larger steps and higher heating rates, as can be seen in figures 2 and 3.

For the 4 K resistometry, the time requirements of the experiment are different, since only short annealing times—some minutes—above the helium bath can be used. We performed five minute isochronal anneals that yielded equilibrium states above about 900 K for $Co_{30}Pt_{70}$.

Under these experimental conditions it is not possible for $Ni_{30}Pt_{70}$ to obtain either *in situ* or 4 K resistivity curves corresponding to equilibrium states in the ordered phase. As we shall see in the next section, however, this point is of minor importance in the
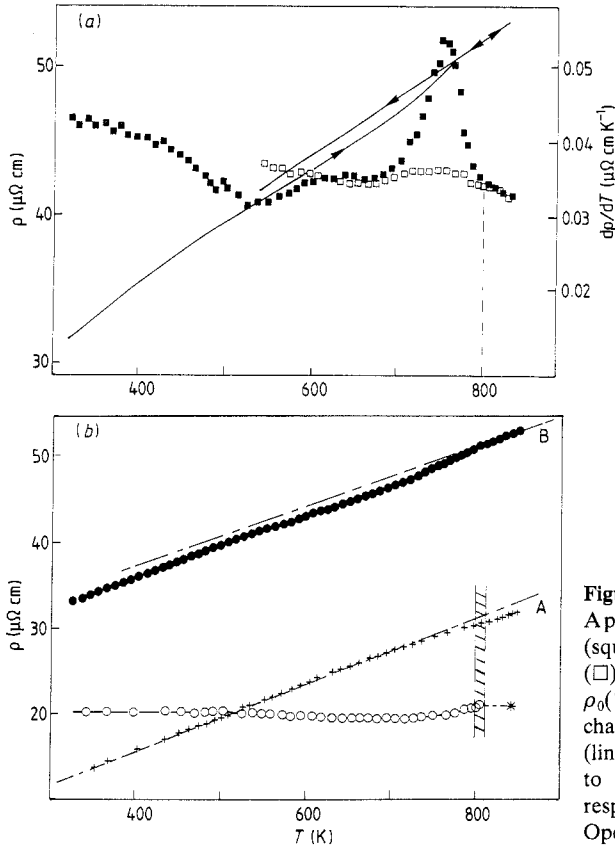
Figure 2. Ni$_{30}$Pt$_{70}$ resistivity and its analysis. (*a*) A plot of $\rho(T)$ (full curves) and of its derivative (squares) for increasing (■) and decreasing (□) temperatures. (*b*) A plot of $\rho(T)$ (●) and $\rho_0(T)$ (○, ∗) and of their difference (+). The chain lines are least-squares fits of $\rho_{ph}^O = A^O T$ (line A) and $\rho^D = \rho_0^D + A^D T$ (line B) according to equations (2). The hatched area corresponds to the O–D transformation region. Open circles show $\rho_0(\eta(T_A))$.

present case, because the residual resistivity difference between the most highly ordered state and the totally disordered one is very small in this alloy (table 2).

4. Results, analysis and discussion

Residual resistivity values measured in the two extremal order states that could be attained are collected together in table 2.

In situ resistivity and its derivative for increasing and decreasing temperatures in Ni$_{30}$Pt$_{70}$ are shown in figure 2(*a*). At the beginning of the measurement, the alloy was in the ordered state attained at the end of the annealing treatment described in § 2 and frozen in by the quench. As expected from the previous kinetics study, the temperature dependence of ρ is reversible only in the disordered phase above 800 K and the ordering process cannot take place *in situ* during the cooling. On the low-temperature side below 550 K, the departure of the derivative curve from a nearly constant value can be attributed to some atomic rearrangements induced by the mobility of supersaturation vacancies, frozen in by the quench from 733 K.

In figure 2(*b*) the high-temperature part of the resistivity is compared with its residual counterpart ($\rho_0(T_A)$) which represents the contribution of the chemical disorder. $\rho_0(T_A)$ remains nearly constant and equal to about 19–20 $\mu\Omega$ cm up to 750 K, and then increases
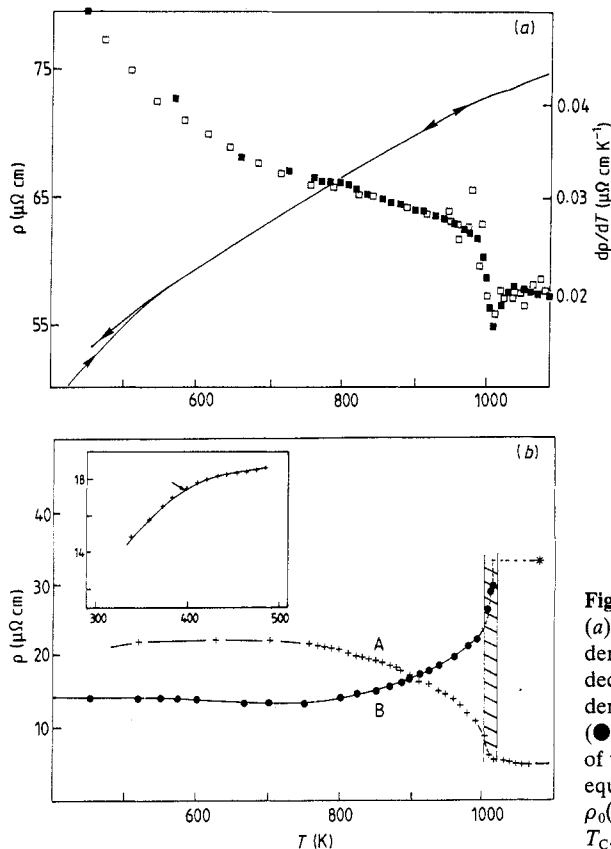
Figure 3. $Co_{30}Pt_{70}$ resistivity and its analysis. (*a*) A plot of $\rho(T)$ (full curves) and of its derivative (squares) for increasing (■) and decreasing (□) temperatures. (*b*) The dependence on T of the measured residual resistivity (●, *) versus the annealing temperature, and of the magnetic term $(\rho_m(T))$ deduced from equation (4). Key: curve A, $\rho_m(T)$; curve B, $\rho_0(\eta(T_A))$. The arrow in the inset indicates T_C.

slightly to 21 $\mu\Omega$ cm in the disordered state. A small decrease is observed around 500 K. We believe that this has the same origin as that observed on the $\rho(T)$ curve, since it is not visible in the difference $(\rho(T) - \rho_0(T_A))$. Hence, in the ordered state, this difference plotted versus T is a straight line, nearly proportional to T, as expected from an electron–phonon diffusion process at high temperature. A least-squares fit of this difference to a linear function $(aT + b)$ yields, between 350 and 750 K, $a = 0.039 \pm 0.005$ $\mu\Omega$ cm K^{-1} and $b = 0.35 \pm 0.15$ $\mu\Omega$ cm. The value of b is negligible compared with the high value of the residual resistivity and of its uncertainty (± 1 $\mu\Omega$ cm), so in the ordered state the differential term is really a phonon-like term $A^O T$ and the total resistivity can be written as

$$\rho^O(T) = \rho_0^O(\eta(T^A)) + \rho_{ph}^O \tag{2a}$$

with

$$\rho_{ph}^O = A^O T \qquad A^O = 0.039 \ \mu\Omega \ \text{cm K}^{-1}.$$

In the disordered state, the dependence on T of the total resistivity is linear, giving

$$\rho^D(T) = \rho_0^D + A^D T \tag{2b}$$

and this fits with $\rho_0^D = 22.6$ $\mu\Omega$ cm and $A^D = 0.031$ $\mu\Omega$ cm K^{-1}. Considering the small temperature interval of the fit (790–850 K) and the broad extrapolation range towards
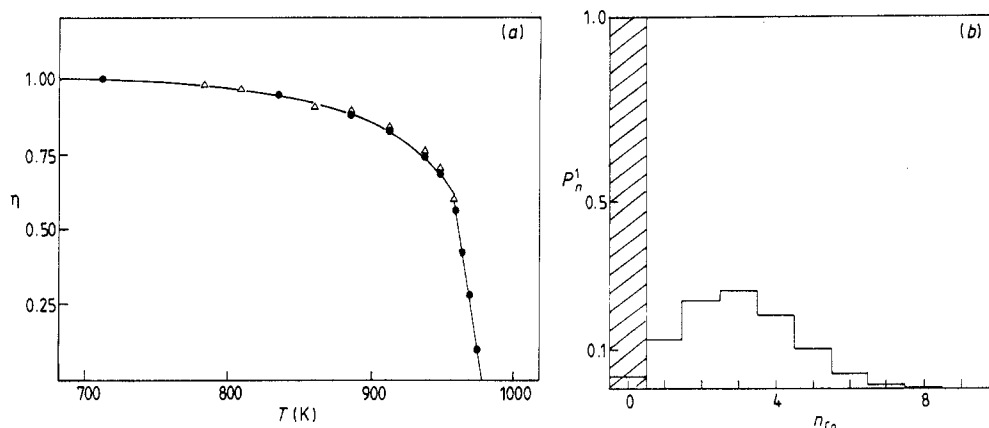
Figure 4. (*a*) The dependence on T of the LRO parameter in single-crystal (●) and poly-crystalline (△) CoPt$_3$ as measured by Berg and Cohen (1972). (*b*) The probability P_n^1 of Co atoms of having n Co atoms in their nearest-neighbour shell in the CoPt$_3$ ordered state (hatched area) and in its disordered state as deduced from a binomial law.

0 K, the extrapolated value obtained ($\rho_0^D = 22.6$ $\mu\Omega$ cm) can be considered as being in good agreement with the value measured directly at 4 K in the quenched-in disordered alloy (21.2 $\pm$ 1 $\mu\Omega$ cm).

Hence, we can conclude that, in both ordered and disordered states of Ni$_{30}$Pt$_{70}$, the resistivity is the sum of a phonon term ($A^{O,D}T$) and of a chemical disorder term ($\rho_0^{O,D}$), which depends on the LRO parameter in the ordered state.

The resistivity curve of Co$_{30}$Pt$_{70}$ and its derivative, obtained by using a heating and cooling rate of 5 K h^{-1} above 750 K, are shown in figure 3(*a*). The total resistivity is hardly affected by the O–D transformation, but this is not the case for its derivative, which displays a strong variation around 1000 K. At lower temperature, not shown on the picture, a change in the $\rho(T)$ slope is observed in the vicinity of 390 K, which corresponds to the Curie temperature (T_C). Comparing the total resistivities of Ni$_{30}$Pt$_{70}$ and Co$_{30}$Pt$_{70}$ alloys in their paramagnetic states, it becomes evident that, at a given temperature, the resistivity is higher by about 15 $\mu\Omega$ cm in Co$_{30}$Pt$_{70}$ than in Ni$_{30}$Pt$_{70}$. Assuming that, as in the previous study of the equi-atomic phases, the high resistivity of Co$_{30}$Pt$_{70}$ has a magnetic origin, we analyse the total resistivity in terms of three contributions, $\rho_0^{O,D}(\eta(T_A))$, $\rho_{ph}^{O,D}$ and $\rho_m^{O,D}$, the last term being the contribution of the spin-disorder scattering by the electron conductions as defined in I. Hence, we have in both ordered and disordered states of Co$_{30}$Pt$_{70}$

$$\rho^O(T) = \rho_0^O(\eta(T_A)) + A^O T + \rho_m^O(T) \tag{3a}$$

$$\rho^D(T) = \rho_0^D + A^D T + \rho_m^D(T). \tag{3b}$$

The measured dependence on T of $\rho_0^{O,D}$ is shown in figure 3(*b*). At low temperature, one observes a constant value of 14 $\mu\Omega$ cm as long as the LRO parameter shown in figure 4(*a*) remains constant. Between 800 and 1010 K, ρ_0^O increases from 14 to 33 $\mu\Omega$ cm, its value in the disordered state. As already indicated in table 2, the residual resistivity difference between the ordered and disordered states ($\Delta\rho^{O-D}$) is clearly larger in Co$_{30}$Pt$_{70}$ than in Ni$_{30}$Pt$_{70}$. There are several possible origins of this. A possible reason we invoke to explain this difference partially is that, in disordered Co$_{30}$Pt$_{70}$ alloys, Nordheim's rule

is not obeyed, as illustrated in figure 6 of I, and the maximum of the $\rho_0(c_{Pt})$ curve is close to $c_{Pt} = 70\%$.

In order to separate the magnetic contribution we proceed as in I, assuming that the phonon coefficients $A^{O,D}$ are equivalent in both Ni–Pt and Co–Pt phases of the same composition. In addition to arguments already invoked in I to justify such an hypothesis, we add that as the phases investigated here are richer in Pt than those studied in the previous work, the role played by Ni or Co elements in the vibrational properties is even less important. The magnetic term $\rho_m^{O,D}$, shown in figure 3(b), is deduced from the relation

$$\rho_m^{O,D} = \rho^{O,D}(T) - \rho_0^{O,D}(T_A) - A^{O,D}T \tag{4}$$

where $\rho^{O,D}$ and $\rho_0^{O,D}$ are the measured quantities, and $A^{O,D}$ are the values determined for $Ni_{30}Pt_{70}$. The low-temperature part of ρ_m, displaying the behaviour around T_c, is shown inset. As expected for a spin-disorder scattering term, ρ_m increases in the ferromagnetic range up to its maximum value at T_c. In the paramagnetic range, ρ_m is constant up to 700 K and then decreases to T_{O-D}, attaining a nearly constant value in the disordered phase.

Comparing the curves showing $\rho_m(T)$, $\rho_0(\eta(T_A))$ and $\eta(T)$ (figure 4(a)) it is clear that, when the LRO parameter decreases, the chemical disorder term increases and the spin-disorder scattering term decreases, by as much as a factor of three between the most ordered state and the disordered one. Thus an interpretation of the $\rho_m(T)$ curve similar to that proposed in I is still valid: the increase of the chemical disorder enhances the Co–Co coordination which in turns enhances the short-range magnetic correlations, as a consequence of which there is a decrease of the moment disorder and of its contribution to the resistivity. An increase of the paramagnetic susceptibility at the O-D transformation of $CoPt_3$ has been previously observed by Dahmani (1985), thus showing the enhancement of magnetic correlations due to the chemical disorder.

A comparison of the present result with the one previously obtained for CoPt yields some further interesting points.

(i) The values we obtained for ρ_m^{max} in, respectively, CoPt and $Co_{30}Pt_{70}$, are 28 and 21 $\mu\Omega$ cm, thus being higher for CoPt than in $Co_{30}Pt_{70}$, as also the average magnetic moments are $1.195\mu_B$ in CoPt and $0.769\mu_B$ in $Co_{30}Pt_{70}$ (Dahmani 1985, Sanchez *et al* 1988). This trend is what one expects for the magnetic contribution to the resistivity in a simple localised magnetism model (see Kasuya (1956) and references in I). Moreover, in $Co_{30}Pt_{70}$, over a broad T range (400–800 K) where $\eta(T)$ is constant, ρ_m keeps a constant value as is also expected for the spin-disorder term of a paramagnetic state in the same model. Such behaviour could not be observed previously for CoPt, for which the Curie temperature is much higher and is close to the region where $\eta(T)$ decreases.

(ii) From its maximum value in the ordered state to its value above T_{O-D}, ρ_m decreases by about a factor of three in $Co_{30}Pt_{70}$, compared with a factor of only two in CoPt. Already mentioned in I, this could be due to some configurational effect: as expected from statistical considerations, the effect of chemical disorder on the Co nearest-neighbour environments—i.e. on short-range magnetic correlations—is more important in $CoPt_3$ (figure 4(b)) than in CoPt (figure 12 of I).

5. Conclusions

The *in situ* and 4K resistivities of non-magnetic $Ni_{30}Pt_{70}$ and magnetic $Co_{30}Pt_{70}$ have been measured with the compounds in their ordered and disordered states, and they are

compared. The measurements were performed by taking into account present or previous ordering kinetics data, in order to get, as far as possible, resistivity values corresponding to well defined thermodynamic states. Whereas the resistivity of Ni$_{30}$Pt$_{70}$ can be analysed as a sum of a chemical disorder term and a phonon-like term, the resistivity of Co$_{30}$Pt$_{70}$ contains a further important contribution which has a magnetic origin. The amplitude and the dependence on T of this term are qualitatively described in the frame of a localised magnetism model in which the short-range magnetic correlations are enhanced by the chemical disorder. All the data compare very well with those from a previous comparative study of equi-atomic NiPt and CoPt alloys. For the second time the presence of short-range magnetic correlations in the paramagnetic state of a Co–Pt alloy and their coupling to the atomic distribution are pointed out on the basis of an investigation of the resistivity.

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