

Magnetic properties and chemical ordering in Co-Pt

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 491

(<http://iopscience.iop.org/0953-8984/1/2/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 16:58

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Magnetic properties and chemical ordering in Co–Pt †

J M Sanchez‡, J L Morán-López§, C Leroux|| and M C Cadeville||

‡ Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA

§ Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, SLP, Mexico

|| Institut de Physique et Chimie des Matériaux, Groupe d'Etude des Matériaux Métalliques, 67070 Strasbourg Cédex, France

Received 23 August 1988

Abstract. The interplay between magnetic properties and chemical ordering in the $\text{Co}_{1-x}\text{Pt}_x$ system is investigated theoretically and experimentally. Experimental results for the Curie temperature, magnetisation and paramagnetic susceptibility in ordered and disordered states are discussed within the framework of statistical models. We show that the magnetic moments on Pt atoms depend sensitively on the local chemical environment. A complete equilibrium phase diagram is also calculated and compared with the experimental data.

The importance of spatial ordering in determining the magnetic properties of alloys has been recognised for many years. For example, it is now well established that the Curie temperature of a disordered alloy may differ considerably from that of a partially ordered system [1]. Conversely, magnetism also influences chemical ordering and the equilibrium phase diagram, introducing substantial changes in the location and width of two-phase regions [2].

Owing to various experimental and theoretical difficulties [3], systematic studies of the interdependence of chemical and magnetic ordering are limited to a few alloy systems [1]. Here we present a detailed investigation of the magnetic and spatial properties of $\text{Co}_{1-x}\text{Pt}_x$ alloys. Our study clearly shows that the magnetic moment of Pt atoms in Co–Pt alloys depends sensitively on the concentration and local chemical environment. We present experimental results for the Curie temperature, magnetisation and paramagnetic susceptibility of ordered and disordered states. These results are analysed using a statistical model solved in the tetrahedron approximation of the cluster variation method (CVM) [4]. The same model is used to compute the magnetic and chemical equilibrium phase diagram, which is compared with our data and with previously determined chemical phase boundaries [5–7] and Curie temperatures [8–10] for disordered alloys.

The Co–Pt system crystallises in the FCC structure (A1). At temperatures above 1400 K, the paramagnetic A1 phase is stable for all concentrations. For temperatures around 1400 K and on the Co-rich side, the system orders ferromagnetically but stays atomically disordered. An ordered Co_3Pt phase (L1_2) has been reported [5–7] to occur with a congruent temperature of approximately 840 K. At $x = 0.5$, a CoPt phase (L1_0)

† This Letter was originally published in *Journal of Physics C: Solid State Physics* (volume 21, issue 33, pages L1091–6) in error.

is observed with a maximum ordering temperature of 1100 K. Furthermore, a CoPt_3 phase ($L1_2$) occurs with a maximum ordering temperature of 1000 K. Both the CoPt and CoPt_3 phases are paramagnetic at high temperatures and become ferromagnetically ordered at lower temperatures.

The emphasis of our study is on the experimental and theoretical characterisation of the effect of chemical short- and long-range order on the magnetic properties of Co–Pt alloys. To this effect we have measured the Curie temperatures (T_C) and the average saturation magnetisation ($\bar{\mu}$) for ordered states obtained at low temperatures after a long time anneal, and for disordered states obtained by rapidly quenching the alloy from the A1 phase. Previous measurements of atomic relaxations and ordering kinetics [11, 12] were used in order to optimise the annealing time and temperature for the ordered samples, and the quenching temperature (1200 K) and quenching rate for the disordered alloys. Single-phases (A1, $L1_2$, $L1_0$) and two-phase regions (A1 + $L1_2$, $L1_2$ + $L1_0$) were determined using x-ray diffraction, transmission electron microscopy and resistivity measurements, as described in [7] and [11].

Our experimental results for the Curie temperature of ordered and disordered phases are indicated in figure 1. Also shown in the figure are data points for the disordered state obtained by Crangle and Pearson [9] for Co-rich ($x < 0.15$) and by Crangle and Scott [10] for Pt-rich ($x > 0.8$) alloys. We see from figure 1 that there is a marked increase in the Curie temperature with disorder.

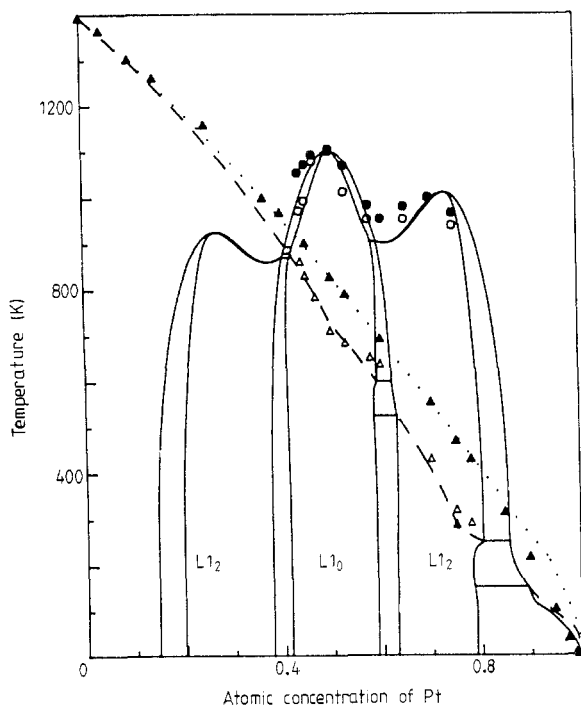


Figure 1. The phase diagram for $\text{Co}_{1-x}\text{Pt}_x$. The calculated order–disorder phase diagram is shown by the full curves and the experimental results by the full and open circles. The calculated Curie temperatures are shown by dotted (random) and broken (equilibrium) curves. The corresponding experimental results are shown by full and open triangles.

Magnetisation measurements were carried out at 4 K using the classical extraction method. External fields of 45 kG were generally sufficient to saturate the magnetisation, except for the CoPt phase, which presents a strong magneto-crystalline anisotropy. In that case, magnetic fields H of up to 150 kG were not sufficient to align the magnetic moments completely and the extrapolation law $\bar{\mu}(H) = \bar{\mu}(1 - b/H^2)$ was used in order to obtain the saturation moment $\bar{\mu}$. Measured values of $\bar{\mu}$ as a function of concentration are shown in figure 2. Several experimental studies [13–15] indicate that the magnetic moment of Co (μ_{Co}) in $\text{Co}_{1-x}\text{Pt}_x$ alloys remains essentially constant. In that case, the average moment on Pt atoms ($\bar{\mu}_{\text{Pt}}$) can be deduced from our magnetisation measurements. We find that $\bar{\mu}_{\text{Pt}}$ depends on alloy composition, as indicated by the open diamonds in figure 2. Such a concentration dependence of $\bar{\mu}_{\text{Pt}}$ can be rationalised in terms of a dependence of the magnetic moment of Pt on the atomic environment, i.e. on the degree of long- and short-range order.

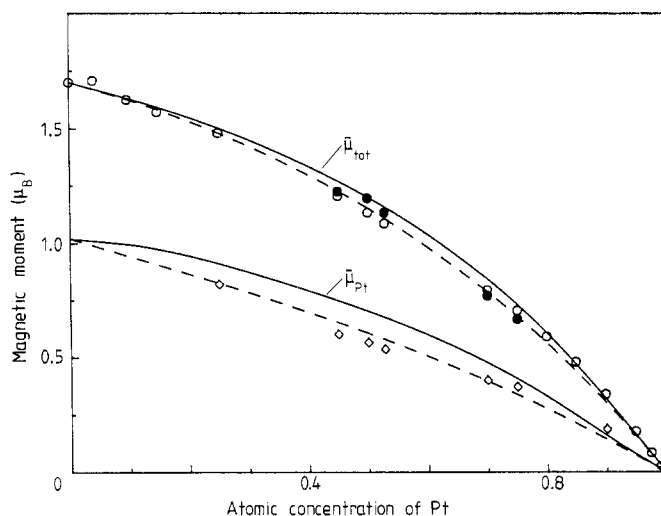


Figure 2. The concentration dependence of the average magnetic moment and the magnetic moment at a Pt atom. The full (broken) curve corresponds to the equilibrium (random) case at 1200 K. The experimental results for the ordered and disordered phases [6, 9, 10] are shown by the full and open circles, respectively. The open diamonds are Pt moments deduced from the experimental data assuming a constant Co moment.

Paramagnetic susceptibilities (χ) for the two stoichiometric phases CoPt and CoPt_3 were measured as a function of temperature across the order–disorder transformation using a translation balance and an external field of 9 kG. The average heating (cooling) rate was 2 K min^{-1} in the single-phase region, was decreased to 1 K min^{-1} in the vicinity of the transition, and was zero at the transition temperature, until the ordering reaction was completed. Both alloys display (i) Curie–Weiss-type behaviour in the ordered and disordered states, and (ii) an increase in the susceptibility at the transition temperature. Data for the equi-atomic CoPt phase are shown in figure 3.

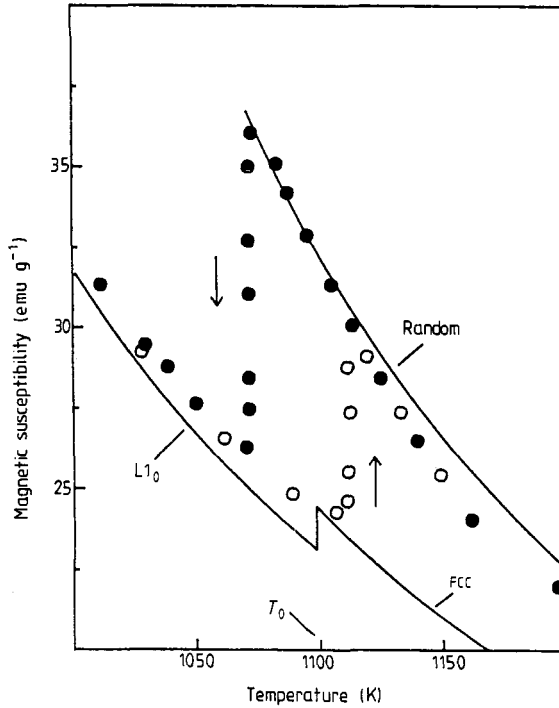


Figure 3. The temperature dependence of the magnetic susceptibility. Calculated results ($\times 1.35$) are shown by the full curve and the experimental data by full and open circles (for cooling and heating, respectively).

The experimental results of figures 1–3 were analysed using a model based on the tetrahedron approximation of the CVM. The expectation value of the chemical energy, H_{chem} , is written in terms of nearest-neighbour (NN) pair interactions V_2 , three-body interactions V_3 corresponding to triangles of NN atoms, and four-body interactions V_4 associated with the NN regular tetrahedron of the FCC lattice:

$$H_{\text{chem}} = V_2 \sum_{ij} \langle \sigma_i \sigma_j \rangle + V_3 \sum_{ijk} \langle \sigma_i \sigma_j \sigma_k \rangle + V_4 \sum_{ijkl} \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle \quad (1)$$

where the occupation number σ_i at lattice site i equals 1 for Co and -1 for Pt atoms, and where the three sums in (1) are carried over all NN pairs, triangles and tetrahedra in the lattice. The three interaction parameters V_2 , V_3 and V_4 are chosen in order to reproduce approximately the temperatures of the congruent points for Co_3Pt , CoPt and CoPt_3 occurring at 840, 1100 and 1000 K, respectively. The three-body interaction V_3 is needed in our model in order to reproduce the asymmetry with composition (i.e. the temperature difference between the congruent points of Co_3Pt and CoPt_3) observed in the experimental phase diagram. We point out that although the magnetic interactions contribute to the phase-diagram asymmetry, their effect is not sufficient to reproduce the experimental data.

The expectation value of the magnetic energy is given in terms of exchange interactions J_{ij} between NN sites i and j by:

$$H_{\text{mag}} = - \sum_{ij} \langle J_{ij} s_i s_j \rangle \quad (2)$$

where the spin operator s_i at site i takes values ± 1 , and where the exchange interactions J_{ij} are expected to depend on the atomic occupancy of sites i and j and on that of neighbouring sites.

In order to calculate the expectation value in (2), we note that each perfectly ordered state γ (Co, Co₃Pt, CoPt, CoPt₃ and Pt) contains only one type of tetrahedron out of the five distinct atomic configurations of the cluster. The expectation value $\langle J_{ij}s_i s_j \rangle$ is calculated self-consistently, using the tetrahedron approximation of the CVM, in terms of the exchange interactions $J_{\sigma\sigma'}^{(\gamma)}$ between pairs of atoms σ and σ' ($\sigma = 1$ and -1 for Co and Pt, respectively) in each of the perfectly ordered structures γ . The $J_{\sigma\sigma'}^{(\gamma)}$ are given, in turn, by the moments $\mu_{\sigma}^{(\gamma)}$ on each atomic species σ in structure γ :

$$J_{\sigma\sigma'}^{(\gamma)} = J\mu_{\sigma}^{(\gamma)}\mu_{\sigma'}^{(\gamma)}. \quad (3)$$

We point out that in addition to Ising-like direct-exchange interactions, the model incorporates other energy contributions via the self-consistent calculation of $\langle J_{ij}s_i s_j \rangle$ in (2). Such contributions to the energy can be interpreted in terms of effective chemical interactions that are dependent on the magnetic state of the system. Thus, our model is formally equivalent to that proposed by Bieber and Gautier [3] who emphasised the inadequacy of the Ising model in the treatment of magnetic transition-metal alloys.

The magnetic moment on a Pt atom in pure Pt is taken to be equal to zero, and that on a Co atom is assumed to be constant and equal to $1.7\mu_B$ for all phases. Thus, the magnetic energy is characterised by four parameters: J , or alternatively the Co–Co exchange interaction in pure Co ($J_{\text{CoCo}}^{(\text{Co})}$), and the magnetic moments of Pt in Co₃Pt, CoPt, and CoPt₃ taken, respectively, equal to $0.6\mu_{\text{Co}}$, $0.45\mu_{\text{Co}}$, and $0.3\mu_{\text{Co}}$. The value of $J_{\text{CoCo}}^{(\text{Co})}$, equal to $139.15 k_B \text{ K}$, was determined from the Curie temperature of pure Co (1394 K), and the values of $\mu_{\text{Pt}}^{(\gamma)}$ were obtained by an approximate fit of our theoretical model to the measured Curie temperatures in the ordered states. A similar fit to the congruent points of the order–disorder transitions gives $V_2 = 3.9 J_{\text{CoCo}}^{(\text{Co})}$, $V_3 = -0.05 J_{\text{CoCo}}^{(\text{Co})}$, and $V_4 = -0.18 J_{\text{CoCo}}^{(\text{Co})}$.

The calculated equilibrium phase diagram is compared in figure 1 with some of the available experimental data for the chemical [7] and magnetic transitions. The full curves in the diagram are the calculated phase boundaries delimiting the first-order transitions between ordered and disordered phases. The full and open circles are experimental values for, respectively, the upper and lower transition temperatures as determined by electrical resistivity measurements, x-ray diffraction and transmission electron microscopy. The calculated equilibrium Curie temperature, indicated by the broken curve, is in excellent agreement with the data of [9] for Co-rich ($x < 0.15$) disordered alloys and with the measurements in ordered states obtained after long time annealing (open triangles). The calculated Curie temperature of alloys without chemical short-range order (random), indicated by the dotted curve in figure 1, is also found to be in excellent agreement with the measured values of T_C (full triangles) for quenched alloys and with the data of [10] for Pt-rich ($x > 0.8$) alloys.

In figure 2 we show the calculated average total magnetic moment and the average moment on a Pt site at 1200 K. For comparison, we also show by broken curves the same quantities for an alloy with complete chemical disorder (random). The difference between the broken and full curves in figure 2 illustrates the effect of short-range order on the magnetic properties of Co–Pt alloys. The experimentally determined average moment is also shown for the ordered [6] (full circles) and the disordered [6, 9, 10] (open circles) phases. We see from the figure that the statistical model is in general agreement with experiment.

Finally, figure (3) shows the calculated magnetic susceptibility for a stoichiometric ($x = 0.5$) Co–Pt alloy in the neighbourhood of the order–disorder transition (1100 K). The figure shows the equilibrium susceptibilities for the disordered (FCC) and ordered ($L1_0$) phases, as well as the susceptibility for the chemically random alloy. The calculated magnetic susceptibilities are in qualitative agreement with the experimental results, although they are a factor of 1.35 smaller than the measured values. In particular, the model correctly predicts a decrease in the magnetic susceptibility upon ordering. However, the magnitude of the discontinuity across the transition for the equilibrium susceptibilities is less than that observed experimentally. Better agreement with the experimental results is obtained if we allow for the fact that, during the susceptibility measurements, the disordered alloy is not in a state of equilibrium short-range order. Thus, an upper limit for the discontinuity in the susceptibility predicted by the model is given by the difference between the random and $L1_0$ susceptibilities at 1100 K.

In conclusion, we have presented measurements of Curie temperatures, magnetic moments and magnetic susceptibilities in $Co_{1-x}Pt_x$ alloys for different degrees of long- and short-range order. The concentration dependence of the average magnetic moment on Pt atoms, obtained assuming a constant moment on Co atoms, is similar to that observed by neutron diffuse scattering in Ni–Pt alloys [16]. The experimental results were analysed using a statistical mechanics model that includes pair and many-body chemical interactions and magnetic exchange interactions that are sensitive to the local chemical environment. The model gives excellent agreement with experimental data for the equilibrium chemical and magnetic phase diagram and with measured Curie temperatures for disordered alloys quenched from high temperatures. In addition we find semi-quantitative agreement between the model and experimental determinations of average magnetic moments and magnetic susceptibilities.

This work was supported by the National Science Foundation through Grants No DMR-8510594 and No INT-8409776, and by Consejo Nacional de Ciencia y Tecnología, Mexico, through Grants No PCCBBEU-022007 and No 140106G202-187.

References

- [1] Cadeville M C and Morán-López J L 1987 *Phys. Rep.* **153** 331
- [2] Dahmani C E, Cadeville M C, Sanchez J M and Morán-López J L 1985 *Phys. Rev. Lett.* **55** 1208
- [3] Bieber A and Gautier F 1986 *J. Magn. Magn. Mater.* **54/57** 967
- [4] Kikuchi R 1951 *Phys. Rev.* **81** 988
- [5] Inden G 1983 *Mat. Res. Soc. Symp. Proc.* **19** 175
- [6] Dahmani C E 1985 *PhD Thesis* Louis Pasteur University, Strasbourg
- [7] Leroux C, Cadeville M C, Dahmani C E, Inden G, Gahn F and Hintz F *Preprint*
- [8] Cadeville M C, Dahmani C E and Kerr F 1986 *J. Magn. Magn. Mater.* **54/57** 1055
- [9] Crangle J and Pearsons D 1960 *Proc. R. Soc. A* **25** 509
- [10] Crangle J and Scott W R 1965 *J. Appl. Phys.* **36** 921
- [11] Leroux C 1988 *PhD Thesis* Louis Pasteur University, Strasbourg
- [12] Cadeville M C, Leroux C, Pierre-Bohnes V and Dahmani C E 1987 *Springer Proceedings in Physics* vol 10 (Berlin: Springer) p 78
- [13] von Laar B 1964 *J. Physique* **25** 600
- [14] Mezinger F and Paoletti A 1966 *Phys. Rev.* **143** 365
- [15] Tissier B 1977 *Doctoral Dissertation*, USMG, Grenoble
- [16] Parra R E and Cable J W 1980 *Phys. Rev. B* **21** 5495