

THE STUDY OF THE ELECTRONIC STRUCTURE OF CrPt₃ ALLOY BY THE LMTO METHOD

A. SZAJEK

Institute of Molecular Physics of the Polish Academy of Sciences
Smoluchowskiego 17/19, 60-179 Poznań, Poland

(Received October 18, 1991; in final form August 3, 1992)

The *ab initio* self-consistent linear muffin-tin orbital calculations in the atomic sphere approximation have been performed for the ordered CrPt₃ (AuCu₃-type structure) alloy. The band structure and the densities of electronic states are presented. The para- and ferrimagnetic phases were considered. The spin-polarized calculations have confirmed the experimental observation of small antiparallel induced magnetic moment on a platinum atom.

PACS numbers: 65.40.-f, 71.10.+x, 74.20.Fg

1. Introduction

The intermetallic CrPt₃ alloy presents a different magnetic order as compared with other platinum based intermetallic alloys MPt₃ (M = Fe, Co, Mn). All these compounds crystallize in AuCu₃(L1₂)-type structure. The magnetic properties are characterized by a large magnetic moment on 3d transition metal atom and a small induced moment on platinum [1-3]. In the case of CrPt₃ the chromium magnetic moment is also large, 3.37 μ_B , and the induced platinum moment is small, 0.26 μ_B , but antiparallel to the chromium one [4]. The antiparallel moments were also observed in VPt₃ [5].

No first principle self-consistent calculations were performed for CrPt₃ to obtain the band structure. The only results were performed within tight-binding scheme [6] and coherent potential approximation (CPA) formalism [7]. The magnetic moments obtained by Tohyama et al. [6] were 3.62 μ_B for Cr atom and -0.13 μ_B for Pt one.

In this paper we present band calculations performed by self-consistent spin-polarised linear muffin-tin orbitals method in the atomic sphere approximation (LMTO-ASA) [8-10] for the magnetically ordered CrPt₃ alloy. Based on these results we shall discuss the electronic properties of this system: the coefficient γ in the electron contribution to specific heat and the electron-phonon coupling coefficient.

2. Method of band calculations

The calculations were performed for para- and ferrimagnetic phase.

The atomic sphere approximation was used in the LMTO method. The band calculations were performed using the von Barth–Hedin [11] parameterization for the local exchange correlations.

In ASA the Wigner–Seitz cell is replaced by a sphere with radius S . The value of S is determined from the condition $4\pi S^3 n/3 = V$, where V is the volume of the cell and n denotes the number of atoms in the primitive cell. The average sphere radii (the same for chromium and platinum atoms) for our system have been obtained by minimizing the total energy. To minimize the ASA errors the combined correction terms [10] were included in our calculations.

In the band calculations we have included s , p and d states for Cr and Pt. To calculate the starting charge densities we have assumed the following initial atomic configurations: core + $3d^5 4s^1$ for Cr and core + $5d^9 6s^1$ for Pt.

The iterations were performed to self-consistency for the valence electrons only and the convergence was up to the value of 0.1 mRy. The eigenvalues were calculated, in the initial phase, in 84 k -points in the irreducible wedge of the Brillouine zone and the final (last iterations till self-consistent) calculations were performed for 286 k -points. A step size of 0.5 mRy was used while integrating the density of states (DOS). To evaluate DOS the tetrahedron method was used [12, 13].

3. Results and discussion

The experimental lattice constant is in the range of 3.871–3.877 Å [4, 14, 15]. The minimum of the total energy was obtained for $S = 2.895$ a.u. (2.92 a.u. if the spin–orbit coupling was not included) which corresponds to the lattice constant $a = 3.920$ Å (3.954 Å). The difference between the theoretical value and the experimental one is about 1%. The minimum of total energy was found for magnetically ordered structure because the lattice measurements, even at room temperatures, were carried out for this phase. The Curie temperature is 494 K [4]. The minimum of energy for the paramagnetic phase was obtained for $S = 2.89$ a.u. (3.913 Å) which is closer to the experimental value. All results presented below were obtained for S calculated in the low temperature magnetically ordered phase.

Figure 1 presents the band structure along the high symmetry directions in the paramagnetic phase [16]. Comparing DOS presented in Fig. 2 [16] and obtained by Tohyama et al. [5] one can notice that their shape is similar but the numerical values are different. Our values of DOS and number of states (NOS) at the Fermi level are collected in Table I. We should notice a very large contribution of Cr atom (66.5%) to the total DOS at the Fermi level. In comparison, the Mn contribution in MnPt₃ is about 50% [17]. The Fermi level is located in the very sharp peak of DOS for $E_F = -0.0800$ Ry. So $N(E_F)$ is relatively high and is equal to 122.608 states/(Ry unit cell). The large values and rapidly varying DOS near the Fermi energy required careful integration in k -space (286 k -points in 1/48 of Brillouin zone) and using a small step (0.5 mRy) while integrating DOS to estimate E_F .

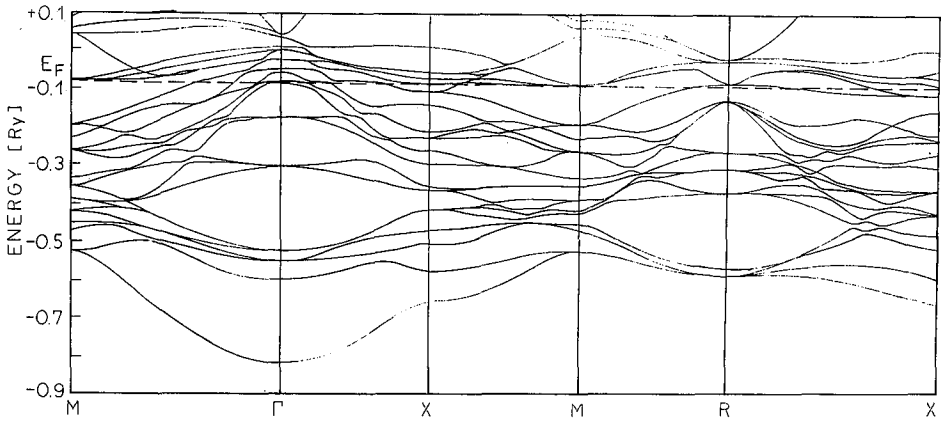


Fig. 1. Dispersion curves along the high symmetry directions for paramagnetic CrPt₃. The broken horizontal line represents the Fermi level.

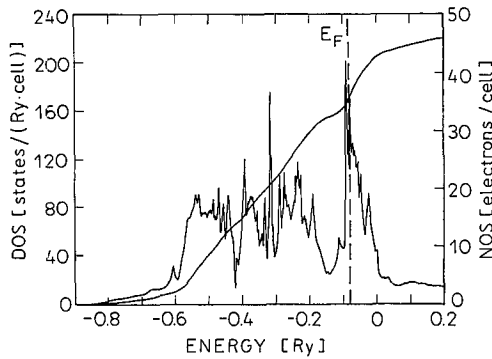


Fig. 2. The total DOS and NOS for the paramagnetic CrPt₃ alloy. The broken vertical line represents the Fermi level.

TABLE I

DOS and NOS at the Fermi level ($E_F = -0.0800$ Ry) in paramagnetic CrPt₃.

| orbital | DOS [states/(Ry cell)] | | | | NOS [electrons/cell] | | | |
|-------------------|------------------------|----------|----------|--------|----------------------|----------|----------|--------|
| | <i>s</i> | <i>p</i> | <i>d</i> | total | <i>s</i> | <i>p</i> | <i>d</i> | total |
| CrPt ₃ | 0.816 | 3.397 | 118.40 | 122.61 | 2.976 | 3.421 | 29.603 | 31.000 |
| Cr | 0.317 | 0.871 | 80.344 | 81.532 | 0.589 | 0.802 | 4.710 | 6.101 |
| 3Pt | 0.499 | 2.526 | 38.051 | 41.076 | 2.387 | 2.619 | 24.893 | 29.899 |

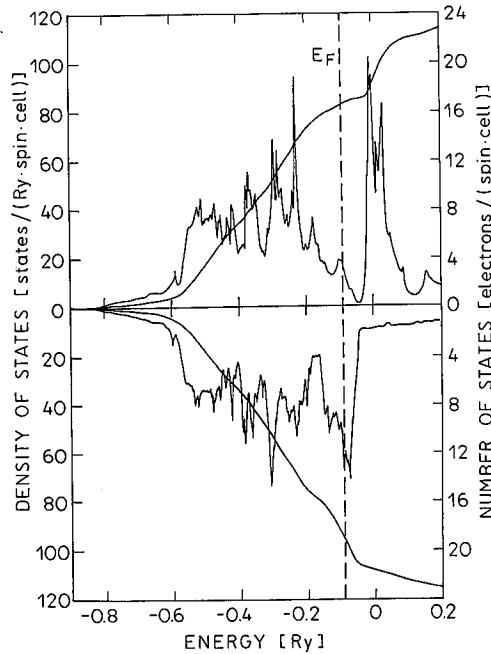


Fig. 3. The total DOS and NOS for two directions of spin in ferrimagnetic CrPt_3 . The broken vertical line represents the Fermi level.

Figure 3 presents DOS of the ferrimagnetic CrPt_3 for majority spin (upper curve) and for minority spin (lower curve). We see that the high peak of paramagnetic DOS moves from the Fermi level to higher energies for majority spin.

TABLE II
DOS and NOS at the Fermi level ($E_F = -0.0922$ Ry) in ferrimagnetic CrPt_3 for two directions of spin (\uparrow and \downarrow).

| orbital | DOS [states/(Ry cell spin)] | | | | NOS [electrons/cell spin] | | | |
|-----------------|-----------------------------|----------------|----------------|--------------------|---------------------------|----------------|----------------|--------------------|
| | $s \uparrow$ | $p \uparrow$ | $d \uparrow$ | total \uparrow | $s \uparrow$ | $p \uparrow$ | $d \uparrow$ | total \uparrow |
| CrPt_3 | 0.731 | 0.856 | 17.439 | 19.026 | 1.501 | 1.685 | 13.349 | 16.535 |
| Cr | 0.614 | 0.104 | 0.875 | 1.593 | 0.287 | 0.389 | 0.998 | 1.674 |
| 3Pt | 0.117 | 0.752 | 16.564 | 17.433 | 1.214 | 1.296 | 12.351 | 14.861 |
| orbital | $s \downarrow$ | $p \downarrow$ | $d \downarrow$ | total \downarrow | $s \downarrow$ | $p \downarrow$ | $d \downarrow$ | total \downarrow |
| CrPt_3 | 0.376 | 1.079 | 54.810 | 56.265 | 1.473 | 1.671 | 16.322 | 19.466 |
| Cr | 0.070 | 0.336 | 24.581 | 24.987 | 0.299 | 0.416 | 3.661 | 4.376 |
| 3Pt | 0.306 | 0.743 | 30.229 | 31.278 | 1.174 | 1.255 | 12.661 | 15.090 |

For minority spin E_F is located in this peak (see Table II for numerical values of DOS and NOS for both directions of spin). The total DOS at the Fermi level is much lower than in the paramagnetic phase and equals 75.291 states/(Ry unit cell).

The calculations confirmed the antiparallel magnetic moment of the platinum atom. Table III contains the partial contribution to the total moment. The moments of the particular atoms are smaller than the moments obtained in the experiment [4] and by tight-binding calculations [6]. The antiparallel alignment of magnetic moments on platinum atoms causes cancelation of resultant moment in the unit cell. Our result, compared to the other theoretical magnetic moments of the unit cell, is closer to the experimental one. The neutron measurements [4] gave the magnetic moment being equal to $2.48 \mu_B$ /unit cell. The magnetic moment obtained by Williams and Jezierski [18] from the low temperature measurements is $2.52 \mu_B$ /unit cell. The theoretical moment of Tohyama et al. [6] is $3.23 \mu_B$ /unit cell. Our calculated value is $2.623 \mu_B$ /unit cell. It is interesting to study the relation between the self-consistent energy-band structure and such ground-state properties as the atomic volume, the compressibility, the crystal structure etc. Let us consider the electronic pressure which is defined as the volume derivative of the total energy: $P = -d\langle\phi|\mathcal{H}|\phi\rangle/dV$. The equilibrium atomic volume is determined by $P(V_0) = 0$. It is possible to decompose P into contribution from each quantum number l . It tells us which electrons try to contract the lattice and which to expand it, i.e. we gain some insight into which electrons are involved in the bonding. In both, paramagnetic and ferrimagnetic, phases the electronic pressure was found to be very close to zero for S giving the minimum of the total energy. $P_{\text{para}} = -70.0$ kbar and $P_{\text{ferri}} = 1.06$ kbar. We see (Table IV) that only d electrons of Cr and Pt take part in bonding of CrPt₃. Other electrons try to expand the lattice. The total contribution of Cr electrons to the pressure is -90.04 kbar and $+92.04$ kbar for Pt electrons.

TABLE III
Total and partial magnetic
moments of particular atoms
[μ_B /atom].

| orbital | Cr | Pt |
|-----------|-------|--------|
| <i>s</i> | 0.016 | -0.014 |
| <i>p</i> | 0.038 | -0.010 |
| <i>d</i> | 2.727 | -0.029 |
| total | 2.781 | -0.053 |
| total [4] | 3.37 | -0.26 |
| total [6] | 3.62 | -0.13 |

The experimental specific heat coefficient γ equals $5.09 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [19]. Our calculated value, from the expression $\gamma_0 = \frac{1}{3}\pi^2 k_B^2 N(E_F)$, equals $3.04 \text{ mJ mol}^{-1} \text{ K}^{-2}$. Using the expression $\gamma = \gamma_0(1 + \lambda)$ one can estimate the

TABLE IV
The total and partial electronic pressures
[kbar] for the ferrimagnetic CrPt₃.

| orbital | <i>s</i> | <i>p</i> | <i>d</i> | total |
|-------------------------|----------|----------|----------|--------|
| Cr ↑ | 6.89 | 10.21 | -81.56 | -64.46 |
| Pt ↑ | 21.38 | 53.75 | -28.11 | +47.02 |
| Cr ↓ | 3.73 | 5.46 | -35.63 | -26.44 |
| Pt ↓ | 12.74 | 45.29 | -13.09 | +44.94 |
| total CrPt ₃ | 44.74 | 114.71 | -158.39 | +1.06 |

electron-phonon coupling parameter λ . In our case the value of λ equals 0.67. The value is very close to that obtained by Jeziński et al. [19] ($\lambda = 0.6$), who used the band model developed by Brouers et al. [20].

The mass enhancement of the conduction electrons due to electron-phonon interaction can be calculated within the Gaspari-Gyorffy formulation [21]. In these calculations *f* electrons have been taken into account. According to McMillan formula [22] one may write the electron-phonon coupling parameter λ in the form [23]

$$\lambda = \frac{1}{N_a} \sum_{i=1}^{N_a} \frac{\eta_i}{M_i \langle \omega^2 \rangle}, \quad (1)$$

where N_a is the number of atoms in the unit cell, M_i is the atomic mass at site *i*, $\langle \omega^2 \rangle$ is the average of the square of the phonon frequency and η_i is the McMillan-Hopfield parameter.

At the low temperatures CrPt₃ is magnetically ordered, therefore we have to take into account the contribution of the electrons with both spin directions. The specific heat measurements and expression $\gamma = \gamma_0(1 + \lambda)$ give an average value of λ . The mass enhancement of electrons is different for different spin directions: $m_s^* = m(1 + \lambda_s)$. The value of γ , usually calculated per mol, depends on contribution of particular fractions of electrons with spin *s*. The average value of η_i is

$$\eta_i = \sum_s c_{is} \eta_{is}, \quad (2)$$

where η_{is} is determined from the Gaspari-Gyorffy formula [21] in the form given by Pettifor [24], c_{is} is the ratio of the number of electrons at site *i* and spin *s* to the total number of electrons at site *i* (c_{is} is calculated using data from Table II, $\sum_s c_{is} = 1$). The values of η are collected in Table V.

The value of $\langle \omega^2 \rangle$ is usually estimated from the Debye temperature, Θ_D . It is a very crude approximation. Recently Skriver and Mertig [25] estimated for rare-earth metals $\langle \omega^2 \rangle^{\frac{1}{2}} = 0.69 \Theta_D$. But when we compare $\langle \omega^2 \rangle^{\frac{1}{2}}$ obtained from neutron scattering with Θ_D we find that the ratio varies from 0.57 to 0.71 for pure metals [26]. The Debye temperature for CrPt₃ equals 328 K [27]. Taking the above values into account we obtain the value of λ in the range of (0.50, 0.77).

We see that the value $\lambda = 0.67$ obtained from the expression $\gamma = \gamma_0(1 + \lambda)$ and the calculated within rigid muffin-tin approximation (RMTA) $\lambda = 0.50 \div 0.77$

TABLE V
Local ($i = \text{Cr, Pt}$) and spin projected
McMillan-Hopfield parameters (η [eV Å⁻²]).

| | Cr | Pt |
|------------------------------------|------------------------|------------------------|
| η_{is} spin \uparrow | 2.784×10^{-5} | 2.493×10^{-2} |
| η_{is} spin \downarrow | 2.773×10^{-1} | 1.684×10^{-1} |
| $\eta_i = \sum_s c_{is} \eta_{is}$ | 2.004×10^{-1} | 9.642×10^{-2} |

are consistent. More accurate estimation of λ needs knowledge of the phonon spectrum to calculate $\langle \omega^2 \rangle$ in Eq. (1).

Acknowledgments

The author is grateful to Prof. J.A. Morkowski and Dr. A. Jezierski for stimulating discussions and for critical reading the manuscript and to Dr. R. Kuentzler for providing some of the experimental data. The calculations were performed using the programs of Dr. N.E. Christensen.

References

- [1] G.E. Bacon, J. Crangle, *Proc. R. Soc. Lond. A* **273**, 387 (1963).
- [2] F. Menzinger, A. Paoletti, *Phys. Rev.* **143**, 365 (1966).
- [3] B. Antonini, F. Lucari, F. Menzinger, A. Paoletti, *Phys. Rev.* **187**, 611 (1969).
- [4] S.K. Burke, B.D. Rainford, D.E.G. Williams, P.J. Brown, D.H. Hukin, *J. Magn. Magn. Mater.* **15-18**, 505 (1980).
- [5] M. Kawakami, T. Goto, *J. Phys. Soc. Jpn.* **46**, 1492 (1979).
- [6] T. Tohyama, Y. Ohta, M. Shimizu, *J. Phys., Condens. Matter* **1**, 1789 (1989).
- [7] A. Jezierski, *J. Phys. F* **13**, L111 (1983).
- [8] O.K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
- [9] O.K. Andersen, O. Jepsen, D. Glötzel, in: *Highlights of Condensed Matter Theory*, Eds. F. Bassani, F. Fumi, M.P. Tosi, North-Holland, New York 1985, p. 59.
- [10] H.L. Skriver, *The LMTO Method*, Springer, New York 1984.
- [11] U. von Barth, L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- [12] O. Jepsen, O.K. Andersen, *Solid State Commun.* **9**, 1763 (1971).
- [13] G. Lehman, M. Taut, *Phys. Status Solidi B* **54**, 469 (1972).
- [14] M.J. Besnus, A.J.P. Meyer, *Phys. Status Solidi B* **55**, 521 (1973).
- [15] T. Goto, *J. Phys. Soc. Jpn.* **43**, 1848 (1977).
- [16] A. Szajek, in: *Proc. 6th Conf. on Physics of Magnetism*, Ed. L. Kowalewski, Adam Mickiewicz University Press, Poznań 1990, Acta Magnetica Suppl. '90, p. 26.
- [17] A. Jezierski, *J. Phys., Condens. Matter* **2**, 493 (1990).
- [18] D.E.G. Williams, A. Jezierski, *J. Magn. Magn. Mater.* **59**, 41 (1986).

- [19] A. Jezierski, R. Kuentzler, D.E.G. Williams, *J. Phys. F, Met. Phys.* **10**, L119 (1980).
- [20] F. Brouers, F. Gautier, J. van der Rest, *J. Phys. F, Met. Phys.* **5**, 975 (1975).
- [21] G.D. Gaspari, B.L. Gyorffy, *Phys. Rev. Lett.* **28**, 801 (1972).
- [22] W.L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- [23] P. Strange, B.L. Gyorffy, *J. Phys. F, Met. Phys.* **16**, 2139 (1986).
- [24] D.G. Pettifor, *J. Phys. F, Met. Phys.* **7**, 1009 (1977).
- [25] H.L. Skriver, I. Mertig, *Phys. Rev. B* **41**, 6553 (1990).
- [26] W.H. Butler, *Phys. Rev. B* **15**, 5267 (1977).
- [27] R. Kuentzler, private communication.