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Tight-binding calculations of the electronic structure and magnetic properties in ordered TPt_3 ($T = \text{Ti, V, Cr, Mn, Fe and Co}$) alloys

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Abstract. Tight-binding-type self-consistent spin-polarised band calculations are performed to study the electronic structure and magnetic properties of ordered TPt_3 ($T = \text{Ti, V, Cr, Mn, Fe and Co}$) alloys with Cu_3Au structure. The global trends of the magnetic moments and low-temperature specific heat coefficients are explained successfully. Ferrimagnetism in VPt_3 and CrPt_3 is explained in terms of the hybridisation between 3d states in the V or Cr band and 5d states in the Pt band. The antiferromagnetic state with collinear magnetic moment on T atoms in the (110) subsheets and with no moment on Pt atoms is shown to be the most stable for FePt_3 among these alloys.

1. Introduction

Ordered TPt_3 alloys ($T = \text{Ti, V, Cr, Mn, Fe and Co}$) have the Cu_3Au -type crystal structure (see figure 1(a)) and exhibit a series of the characteristic magnetic ground state. No systematic study of the magnetic properties of this system has, however, been made on the basis of the band model as far as we know. In this paper therefore we present a systematic investigation of the electronic structure and ground-state magnetic properties of these alloys by using the simple tight-binding (TB) method.

We summarise the experimental results for the magnetic properties of the system in the following way. TiPt_3 has been reported to be paramagnetic (P) (Kuentzler 1981). VPt_3 has been observed to have either TiAl_3 -type or Cu_3Au -type structure and for the latter the spontaneous magnetic moment is $0.1\mu_B$ per formula unit (Jesser *et al* 1981). NMR experiments (Kawakami and Goto 1979) on $\text{V}(\text{Ir}_{1-x}\text{Pt}_x)_3$ have indicated that VPt_3 shows the ferrimagnetic (FI) structure with $m_V = 1.0\mu_B$ and $m_{\text{Pt}} = -0.3\mu_B$, where m_A ($A = \text{Ti, V, Cr, Mn, Fe, Co and Pt}$) is the local moment on atom A. CrPt_3 also shows the FI structure; the magnetic moments were once reported to be $m_{\text{Cr}} = 2.33\mu_B$ and $m_{\text{Pt}} = -0.27\mu_B$ (Pickart and Nathans 1963), but they have recently been revised as $m_{\text{Cr}} = 3.37\mu_B$ and $m_{\text{Pt}} = -0.26\mu_B$ (Burke *et al* 1980). MnPt_3 shows the ferromagnetic (F) structure (Pickart and Nathans 1962, Antonini *et al* 1969); $m_{\text{Mn}} = 3.6\mu_B$ is the largest in the TPt_3 system. FePt_3 shows the antiferromagnetic (AF) structure characterised by the wavevector $2\pi(\frac{1}{2}, \frac{1}{2}, 0)/a$ where a is the lattice constant, in which Fe moments of $m_{\text{Fe}} = 3.3\mu_B$ are aligned ferromagnetically on the (110) subsheets and Pt atoms carry no moment

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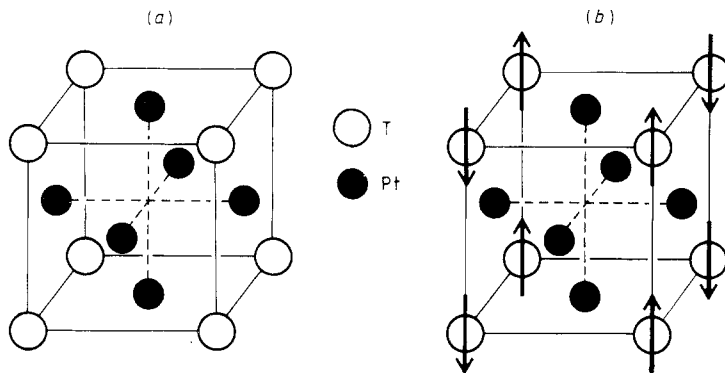


Figure 1. (a) The unit cell of the Cu₃Au-type crystal structure. Open circles and full circles indicate the T (=Ti, V, Cr, Mn, Fe and Co) and Pt atoms, respectively, and (b) the antiferromagnetic structure of FePt₃ ordered alloy. The arrows indicate the observed direction of the magnetic moments on Fe atoms.

(Bacon and Crangle 1963) as shown in figure 1(b). CoPt₃ shows the F structure with $m_{\text{Co}} = 1.64\mu_{\text{B}}$ and $m_{\text{Pt}} = 0.26\mu_{\text{B}}$ (Menzinger and Paoletti 1966).

Some theoretical studies based on the local density or local spin density approximation have so far been made for VPt₃, MnPt₃, and FePt₃. Kübler (1984) has calculated the density of states (DOS) and the magnetic moments for VPt₃ with Cu₃Au structure using the augmented-spherical-wave (ASW) method. His calculation has given $m_{\text{V}} = 1.45\mu_{\text{B}}$ and a total moment of $m_{\text{tot}} = 1.3\mu_{\text{B}}$ per formula unit (FU), but the observed value of the total moment is $0.1\mu_{\text{B}}/\text{FU}$. Hasegawa (1985) has calculated the spin-polarised band structure for MnPt₃ using the augmented-plane-wave (APW) method. The calculated magnetic moments on Mn atoms and Pt atoms have been in good agreement with experiment. Kulikov *et al* (1985) have calculated the paramagnetic band structure for FePt₃ using the linearised hybridised KKR method. They have found the appearance of two types of the spin-density-wave (SDW) states from their band structure calculation and a new model to explain the magnetic properties of Fe_{1+ δ} Pt_{3- δ} has been reported (Kulikov 1985).

In this paper, the TB parametrisation scheme, which is very simple in comparison with the first-principles method of band calculation but can give a qualitative understanding of the magnetic properties of transition metals and alloys, is applied to study the electronic structure of TPt₃ ordered alloys and to examine their characteristic magnetic properties, for instance we study why FI appears in VPt₃ and CrPt₃ and why AF occurs only in FePt₃. The TB method has provided a successful description of the electronic structure and magnetic properties of the TPt system (Ohta *et al* 1989) and many intermetallic compounds (see, for example, Yamada 1988).

The method of calculation and choice of the parameters are presented in § 2. In § 3 the band structures are calculated and the calculated results of the total electronic energy, magnetic moments and the low-temperature electronic specific heat coefficient are compared with the experimental ones. Conclusions are given in § 4.

Table 1. Values of the parameters used for calculation. The number of d electrons on i atom (n_i), the intra-atomic Coulomb integral (U_i), and the lattice constant (a) for TPt_3 (T = Ti, V, Cr, Mn, Fe and Co) alloys are listed.

Constituents	Ti	V	Cr	Mn	Fe	Co	Pt
n_i (atom ⁻¹) ^a	2.90	3.89	4.96	6.02	7.05	8.02	8.74
U_i (mRyd atom) ^b	50	52	56	60	68	72	50 ^c
a (Å)	3.86 ^d	3.87 ^e	3.877 ^f	3.89 ^f	3.87 ^g	3.831 ^h	—

^a Papaconstantopoulos (1986),^b Janak (1977),^c Liu *et al* (1979),^d extrapolated,^e Jesser *et al* (1981),^f Lewis and Williams (1976),^g Crangle and Shaw (1962),^h at 30 at.% Co (Geisler and Martin 1952).

2. Method of calculation

The electronic structure is calculated self-consistently by the combined method of the TB parametrisation scheme of Slater and Koster (1954) and the Andersen–Jepsen–Pettifor type evaluation of the hopping integrals (Andersen and Jepsen 1977, Pettifor 1977). In the paramagnetic state, the effective potential V_i^p on each site i is determined self-consistently so as to satisfy the local charge neutrality. For the calculation of the spin-polarised state, we employ the Hubbard model with the intra-atomic Coulomb interaction between electrons with opposite spins and use the Hartree–Fock approximation. The effective potential with spin σ on the site i may then be written (Yamada and Shimizu 1985) as

$$V_{i\sigma} = V_i^p + U_i(\langle n_{i-\sigma} \rangle - n_i) \quad (1)$$

where U_i is the intra-atomic Coulomb integral and $\langle n_{i-\sigma} \rangle$ is the expectation value of the number of electrons on the site i with $-\sigma$ spin, $n_{i-\sigma}$. The computations are made to search for the self-consistent solutions satisfying equation (1). The charge transfer breaking the local charge neutrality may occur here. In the case where the charge transfer is unreasonably large, we perform another band calculation by readjusting the values of V_i^p so as to satisfy the perfect local charge neutrality. The total electronic energy in the spin-polarised state may be expressed (Ohta *et al* 1989) as the sum of the covalent bond energy E^p in the paramagnetic state and the magnetic contribution E^{mag} . The calculation of the total electronic energy is made without the readjustment of V_i^p because this can lead to an improper evaluation of E^p .

The unit cell in the paramagnetic state is taken to be the simple cubic one (see figure 1(a)), whereas in the spin-polarised (ferro- and antiferromagnetic) states we use the antiferromagnetic $FePt_3$ -type tetragonal unit cell containing two independent Fe atoms and six Pt atoms (cf figure 1(b)) in order to discuss the magnetic phase stability between ferromagnetic and $FePt_3$ -type antiferromagnetic states. The energy eigenvalues for the paramagnetic and spin-polarised states are calculated at the 455 and 252 regular mesh-points in the irreducible wedge of the Brillouin zone, respectively, and the tetrahedron linear interpolation method (Rath and Freeman 1975) is used to evaluate the DOS and local charges.

Only the d orbitals are taken into account for simplicity because the sp electrons are not mainly responsible for the magnetism in d band metals. We also disregard the spin-orbit coupling effects for simplicity. The values of the parameters used for calculation are summarised in table 1. The hopping integrals are included up to the second-nearest

neighbours for T–T and T–Pt pairs and up to the fourth neighbours for Pt–Pt pairs. For T–Pt pairs the geometrical average between the values of T–T and Pt–Pt pairs is assumed. The values of the hopping integrals are estimated by using the d-band mass and Wigner–Seitz radius listed by Andersen and Jepsen (1977). The values of the lattice constant used are all experimental values except for TiPt₃. For the latter we assume an extrapolated value, 3.86 Å, of the observed lattice constants for VPt₃, CrPt₃ and MnPt₃. The numbers of d electrons, n_T and n_{Pt} , used are those obtained for various metals by Papaconstantopoulos (1986), who has fitted the non-orthogonal TB bands to the first-principle APW energy eigenvalues and thereby evaluated the numbers of electrons of s, p, t_{2g} and e_g characters. The values of U_T and U_{Pt} are those calculated by Janak (1977) and Liu *et al* (1979), respectively, within the local spin density approximation.

3. Results of calculation

The calculated DOS curves for TiPt₃ and CrPt₃ in the paramagnetic state are shown in figure 2 and the values of V_i^p are listed in table 2. Associating with the change of T atoms from Ti to Co the position of the Fermi level ϵ_F shifts to the right of the DOS curves. Particularly in FePt₃, ϵ_F lies in the middle of the large higher-energy peak coming mainly from the electrons on T atoms.

The spin-polarised band calculations are carried out self-consistently by using the values of U_i shown in table 1 for each atom. For the calculation of the AF structure, the FePt₃-type magnetic structure is assumed. The calculated results of the local magnetic moments, charge transfer and total electronic energies are listed in table 2. All the alloys have solutions of both F (or FI) and AF type and the most stable magnetic state is obtained by comparing the total energies in P, F (or FI) and AF states. The global trend of the observed magnetic series, P–FI–F–AF–F, is mostly reproduced as shown in table 2.

In TiPt₃ the calculated total energies in P, FI and AF states are of the same values within the computational accuracy, and the obtained magnetic moments in FI and AF states are very small. In this alloy the extrapolated lattice constant is assumed. If we use a reasonably smaller value of the lattice constant, the magnetic moments obtained become smaller because of the decrease in the height of the DOS, and it is confirmed that by only a small percentage decrease in the lattice constant the solution of the spin-polarised states disappears. In this sense the calculated results are consistent with experiment.

In MnPt₃ the most stable magnetic state obtained here is AF, but the observed one is F. The difference between the energies in AF and F states is considerably large. In order to examine the stability of the FePt₃-type AF structure along the series, we also calculate the total energies of the system under the condition that the intra-atomic Coulomb integrals have the same value 50 mRyd in all atoms. Figure 3 represents the difference between the energies in AF and F or FI states along the series from VPt₃ to CoPt₃. It is found there that the AF state is stable in MnPt₃, FePt₃ and CoPt₃, but it is the most stable in FePt₃ among these three. In experiment, only FePt₃ is AF in the TPt₃ system.

The charge transfer induced by the spin polarisation is unreasonably large in MnPt₃, FePt₃ and CoPt₃ as seen from table 2. Hence we also calculate the spin-polarised band structures by readjusting the values of V_i^p to satisfy the local charge neutrality. The calculations are made for VPt₃, CrPt₃, MnPt₃ and CoPt₃ in the F (or FI) state and for FePt₃ in the AF state. The calculated values of the local and total magnetic moments are shown in figure 4. The noticeable experimental features, i.e. the local moment on T

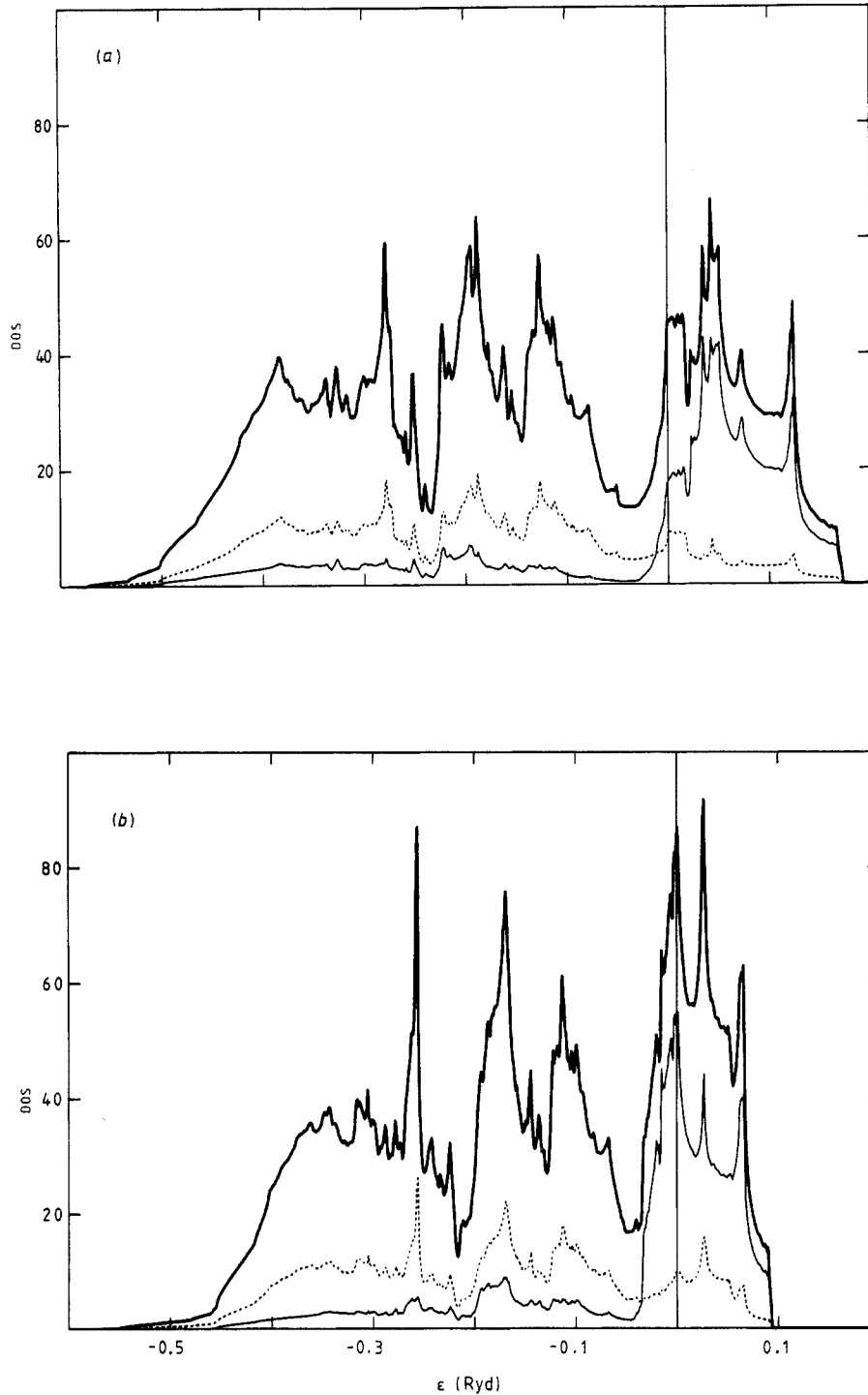


Figure 2. Calculated DOS in the paramagnetic state for (a) $TiPt_3$, (b) $CrPt_3$. Thick full curves denote the total DOS in units of $\text{Ryd}^{-1} (TPt_3)^{-1} \text{spin}^{-1}$ and thin full and broken curves denote the local DOS of T and Pt atoms in units of $\text{Ryd}^{-1} \text{atom}^{-1} \text{spin}^{-1}$, respectively. The thin vertical line denotes the position of the Fermi level.

Table 2. The atomic potentials V_i^P (Ryd) on the site i , local magnetic moments m_T and m_{Pt} (μ_B /atom), charge transfers from T atoms to Pt atoms n_{CT} (T atom $^{-1}$), total electronic energies E (Ryd/FU) and the stable magnetic orders obtained by the theory. The FePt $_3$ -type AF structure is assumed in all AF states.

Alloys	TiPt $_3$	VPt $_3$	CrPt $_3$	MnPt $_3$	FePt $_3$	CoPt $_3$	
Paramagnetic (P)							
V_T^P	-0.0183	-0.0367	-0.0401	-0.0481	-0.0594	-0.0752	
V_{Pt}^P	-0.2018	-0.1969	-0.1893	-0.1824	-0.1826	-0.1834	
E^P	-1.591	-1.377	-1.209	-1.097	-1.016	-0.957	
Ferromagnetic (F or FI)							
m_T	0.14	2.49	3.62	4.24	4.21	2.88	
m_{Pt}	-0.02	-0.15	-0.13	0.14	0.33	0.38	
n_{CT}	0.00	-0.20	0.03	0.49	1.28	0.92	
E	-1.591	-1.402	-1.284	-1.207	-1.138	-1.001	
Antiferromagnetic (AF)							
m_T	0.01	1.97	3.59	4.20	4.13	2.84	
m_{Pt}	0	0	0	0	0	0	
n_{CT}	0.00	-0.16	-0.11	0.40	1.24	0.96	
E	-1.591	-1.387	-1.273	-1.214	-1.145	-1.002	
Magnetic order	P \approx FI \approx AF		FI	FI	AF	AF	F \approx AF

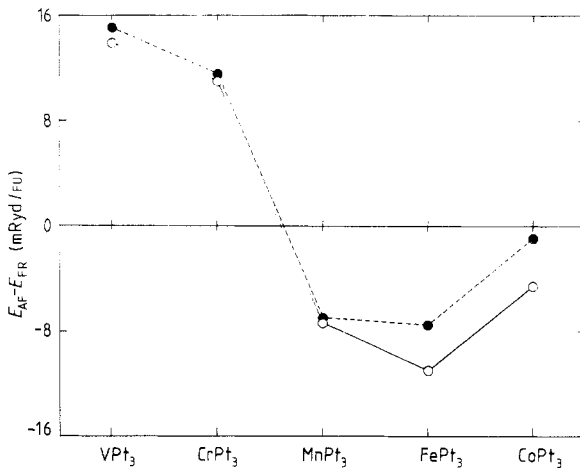


Figure 3. The difference between the total energies in the F or FI state (E_{FR}) and the AF (E_{AF}) state. The calculated values using the intra-atomic Coulomb integrals listed in table 1 are shown by full circles. Open circles denote the results where the value of intra-atomic Coulomb integral 50 mRyd is used for all the constituent atoms.

atoms showing a maximum at MnPt $_3$ in the series and the sign of the Pt moments changing between CrPt $_3$ and MnPt $_3$, are reproduced satisfactorily in the present calculation, whether or not the local charge neutrality condition is satisfied. A better agreement with the experimental results for the local moments on T atoms is obtained under the local charge neutrality condition. The calculated total moment in VPt $_3$, which is similar to the result of the ASW calculation (Kübler 1984), is too large compared with experiment. We thus hope that more theoretical and experimental work will be done for VPt $_3$ alloy with the Cu $_3$ Au structure.

Since the contribution of d states to the DOS is dominant near ϵ_F in these alloys, we can compare the calculated values of the low-temperature electronic specific heat

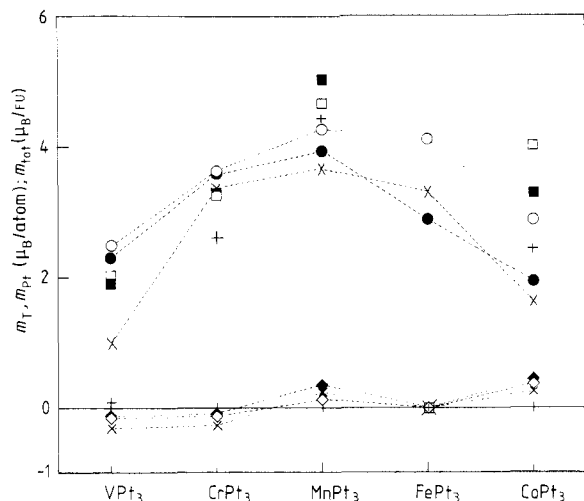


Figure 4. Calculated and experimental values of the local and total magnetic moments in TPt_3 ($T = V, Cr, Mn, Fe$ and Co) ordered alloys. The symbols \circ , \diamond and \square indicate the calculated values of m_T , m_{Pt} and m_{tot} , respectively, listed in table 2 without satisfying the local charge neutrality condition. The symbols \bullet , \blacklozenge and \blacksquare also indicate the calculated values of m_T , m_{Pt} and m_{tot} , respectively, under the local charge neutrality condition. The symbols \times and $+$ indicate the experimental values of the local and total magnetic moments, respectively, for VPt_3 (Kawakami and Goto 1979, Jesser *et al* 1981), for $CrPt_3$ (Burke *et al* 1980, Williams and Lewis 1979), for $MnPt_3$ (Antonini *et al* 1969), for $FePt_3$ (Bacon and Cranage 1963) and for $CoPt_3$ (Menzinger and Paoletti 1966). In $FePt_3$ all the values of m_{Pt} and m_{tot} are zero.

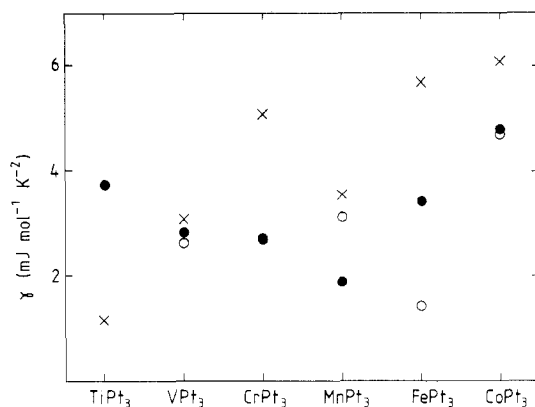


Figure 5. Calculated values (\bullet) with and (\circ) without satisfying the charge neutrality condition and experimental values (\times Kuentzler 1981) of the electronic specific heat coefficient γ of TPt_3 alloys.

coefficient γ obtained from our DOS with the observed ones. All the calculated values of γ are smaller than the observed ones (Kuentzler 1981) except in $TiPt_3$, as shown in figure 5. The difference is considered to be due mainly to the contribution from the electron-phonon interaction. The trends of the experimental values along the series from $CrPt_3$ to $CoPt_3$ are reproduced satisfactorily when the local charge neutrality is satisfied. Although the preliminary calculation for $TiPt_3$ with the 5% smaller lattice constant gives a 20% smaller value, $3.0 \text{ mJ mol}^{-1} \text{ K}^{-2}$, this is also too large compared with the experimental value, $1.15 \text{ mJ mol}^{-1} \text{ K}^{-2}$ (Kuentzler 1981). To get a better agreement we need fine adjustments of the parameter n_{Ti} , because ϵ_F in the paramagnetic state is just on the shoulder of a small peak of the DOS, as shown in figure 2(a).

The spin-polarised DOS curves for the series with the local charge neutrality condition are shown in figure 6. The local DOS of T atoms has a large exchange splitting while that of Pt atoms has a quite small exchange splitting. This explains the large local moments on T atoms and the small local moments on Pt atoms.

The occurrence of FI in VPt_3 and CrPt_3 is explained as follows. The 5d states on Pt atoms lie on the lower-energy side of the 3d states on T atoms. In the spin-polarised states of T atoms the 3d bands with up and down spins shift toward the lower- and higher-energy sides, respectively. Then the hybridisation between the 3d and 5d states with up spin becomes stronger than that with down spin. When the number of d electrons on T atoms is not more than that on Cr atoms, the integrated value of the local DOS at the Pt site with up spin from ϵ_F to the top of the DOS, i.e. the number of d holes on a Pt atom with up spin, becomes larger than that with down spin. Then the magnetic moment on Pt atoms becomes negative or opposite in direction to that on V and Cr atoms. In MnPt_3 which is F, on the other hand, the number of d holes on a Pt atom with up spin becomes smaller than that with down spin, because the 3d states with up spin on a Mn atom are almost occupied as shown in figure 6(c). In the present VPt_3 and CrPt_3 alloys, therefore, the origin of FI is explained by the hybridisation between 3d states on the T atom and 5d states on the Pt atom, the resultant hybridised band being associated with the appropriate number of d electrons on T atoms.

4. Conclusions

In this paper, TB-type self-consistent band calculations have been performed for the TPt_3 ordered alloys with the Cu_3Au structure within the Hartree–Fock approximation of the Hubbard model for their spin polarisation. The present TB method, which is much simpler in comparison with the first-principles local density band calculations, has straightforwardly brought us the qualitative understanding of the magnetic properties of these alloys. First it has been shown that the antiferromagnetic structure with the wavevector Q_1 is most stable for FePt_3 among TPt_3 ordered alloys. Secondly the ferromagnetism in VPt_3 and CrPt_3 has been explained qualitatively in the framework of the band model containing the d orbitals only. Finally the observed global trends of the magnetic moments on each atom and the low-temperature specific heat coefficients in the TPt_3 series have been reproduced successfully, especially when the local charge neutrality is satisfied.

The TB method employed in this paper is very simple and useful for the qualitative understanding of the electronic structure and magnetic properties of transition metals, alloys and compounds where the d electrons are considered to play dominant roles. For more quantitative discussions within the TB framework, we should include the s–d hybridisation and spin–orbit coupling effects considered to be significant for the Pt system.

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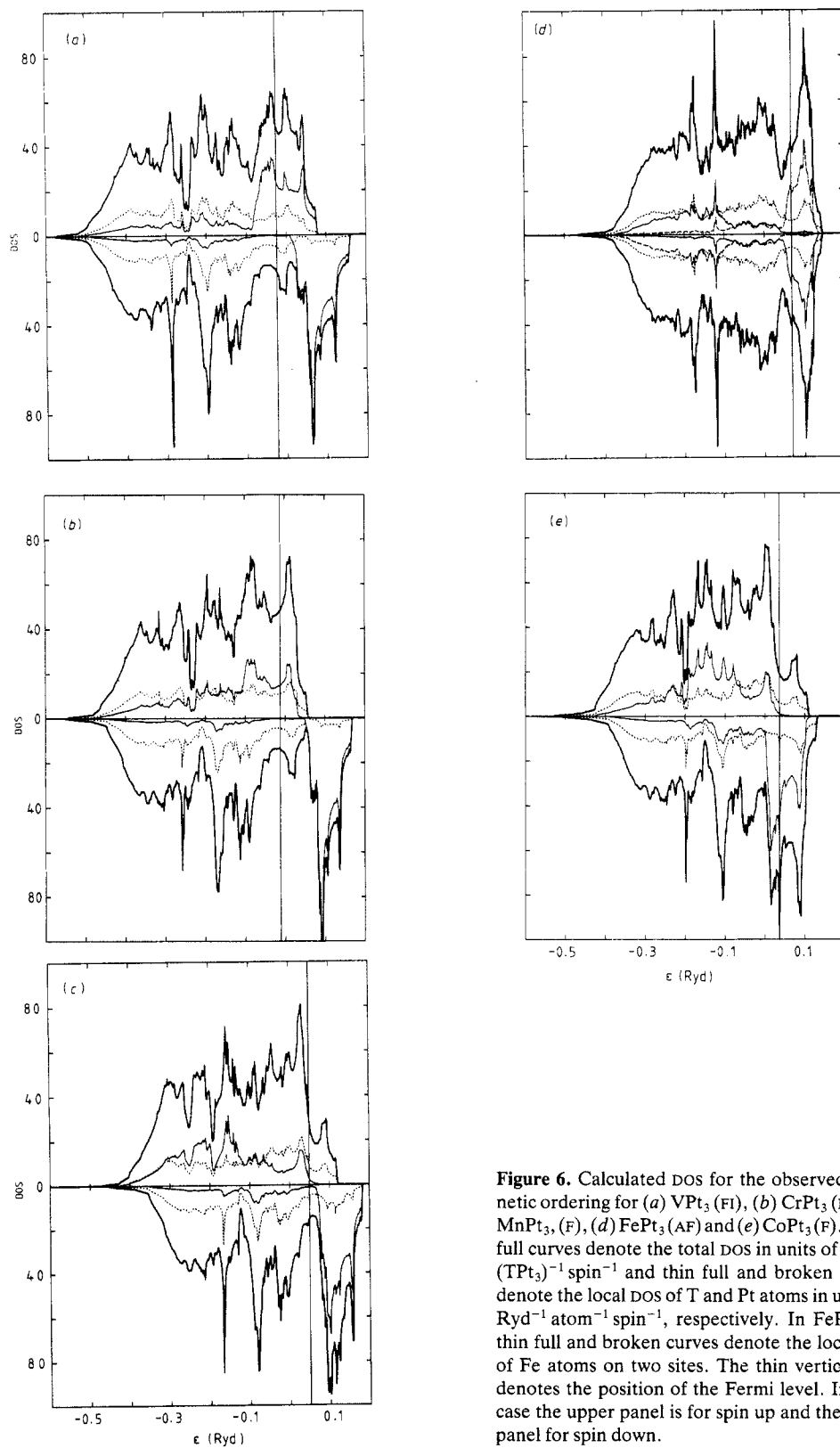


Figure 6. Calculated DOS for the observed magnetic ordering for (a) VPt_3 (FI), (b) $CrPt_3$ (FI), (c) $MnPt_3$ (F), (d) $FePt_3$ (AF) and (e) $CoPt_3$ (F). Thick full curves denote the total DOS in units of $\text{Ryd}^{-1} (TPt_3)^{-1} \text{spin}^{-1}$ and thin full and broken curves denote the local DOS of T and Pt atoms in units of $\text{Ryd}^{-1} \text{atom}^{-1} \text{spin}^{-1}$, respectively. In $FePt_3$ the thin full and broken curves denote the local DOS of Fe atoms on two sites. The thin vertical line denotes the position of the Fermi level. In each case the upper panel is for spin up and the lower panel for spin down.

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