

# ELECTRONIC STRUCTURE OF $Pt_{1-x}Mn_x$ AND $Pt_{1-x}Cr_x$ DISORDERED ALLOYS

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Electronic density of states of disordered fcc  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  alloys for  $0 < x < 0.35$  is calculated by the tight-binding linear muffin-tin orbital (TB LMTO) and the coherent potential approximation (CPA) method. Using the Stoner model it was found that the disordered Pt-Mn and Pt-Cr alloys are paramagnetic.

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## 1. Introduction

The intermetallic Pt-Mn and Pt-Cr alloys belong to the group of compounds in which the crystallographic ordering influences strongly the magnetic properties. These compounds near the  $L1_2$  ( $Cu_3Au$ ) ordered phase were intensively examined experimentally and theoretically [1-13]. From the phase diagram of Pt-Mn compound (Fig. 1 in [1]) it follows that up to 0.15 at % Mn the system has fcc-type structure and then for  $x_{Mn} < 0.38$  it crystallizes in the ordered  $Cu_3Au$ -type structure. The lattice parameter  $a$  (Fig. 2a in [1]) is constant up to  $x_{Mn} = 0.38$ .

In the case of Pt-Cr alloys the lattice parameter slowly decreases with the increase in Cr concentration (Fig. 2 in [1]).  $Pt_{1-x}Cr_x$  system has the fcc-type structure in the broad region of Cr concentration. The magnetic moment in Pt-Mn and Pt-Cr alloys depends strongly on the distribution of Mn, Cr and Pt atoms in the lattice. The measurements [1] indicate that the magnetic moment exists only in the completely ordered system with the  $L1_2$ -type structure. The small deviation from the stoichiometry leads to the decrease in the magnetic moment [1]. In this paper we study the electronic structure and the magnetic properties of the disordered Pt-Mn and Pt-Cr alloys.

Electronic and magnetic behaviour of  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  are similar for  $x < 0.35$ . The manganese atom has only one  $d$ -electron more than chromium and the values of their Wigner-Seitz radii are close. The magnetic properties of Pt-Mn and Pt-Cr compounds are mainly due to  $d$ -electrons of Mn or Cr atoms. The direct interaction between Mn(Cr)-Mn(Cr) is antiferromagnetic and it leads

to the decrease in the total magnetic moment. Hence the value of the magnetic moment so strongly depends on the degree of ordering in the system. The ordered  $\text{Cu}_3\text{Au}$ -type structure can be divided into four interpenetrating simple cubic sublattices. One of these sublattices (formed by the corner atoms) is occupied by Mn or Cr atoms and the other three are filled by Pt atoms. Each Mn and Cr atom has twelve nearest neighbour Pt atoms and six next neighbour Mn(Cr) atoms. In this way in the  $\text{Cu}_3\text{Au}$  ( $L1_2$ )-type structure there is no direct interaction between Mn(Cr) and Mn(Cr) atoms in the nearest neighbour distance and this fact can explain the maximum value of the magnetic moment in the ordered structure. In the disordered  $\text{Pt}_{1-x}\text{Mn}_x$  or  $\text{Pt}_{1-x}\text{Cr}_x$  alloys Pt, Mn and Cr atoms are distributed randomly in the lattice with the probabilities proportional to their concentrations. In the case of the partially ordered alloys the local concentration depends on the short-range order parameter  $\alpha$  [13–15].

In this paper we report the electronic structure of the paramagnetic  $\text{Pt}_{1-x}\text{Mn}_x$  and  $\text{Pt}_{1-x}\text{Cr}_x$  disordered alloys. The electronic density of states (DOS) is calculated in the tight-binding linear muffin-tin orbital method and coherent potential approximation (LMTO-CPA) [16, 17]. The magnetic stability of the system is tested using the modern formulation of the Stoner model. In Sec. 2 we briefly summarize the method of calculations of the coherent potentials and of the density of states. The main results (the paramagnetic DOS for Pt-Mn and Pt-Cr alloys) are presented in Sec. 3. Finally we give some conclusions.

## 2. Method of calculations

The electronic structure of the disordered binary alloys can be computed by the recursion method [18] or using the coherent potential approximation. In the last years Andersen et al. [19, 20] formulated the tight-binding version of the LMTO method. Recently Kudrnovský et al. [16, 17] presented the TB LMTO-CPA method for the calculation the electronic structure of the disordered alloys. This method was applied to the calculations of the electronic properties of many disordered systems [21–24]. In this method we can also include the effect of the off-diagonal disorder. The TB LMTO-CPA method is based on the results of the self-consistent linear muffin-tin orbital method. In this paper we calculated the electronic density of states for  $\text{Pt}_{1-x}\text{Mn}_x$  and  $\text{Pt}_{1-x}\text{Cr}_x$  fcc disordered alloys using the TB LMTO-CPA method.

In the tight-binding LMTO representation the first-order Hamiltonian matrix has the two-centre form [16, 17]:

$$H_{RL,R'L'} = C_{RL}\delta_{RR'}\delta_{LL'} + D_{RL}^{1/2}S_{RL,R'L'}D_{R'L'}^{1/2}, \quad (1)$$

where  $C$  and  $D$  are so-called potential parameters and  $S$  is the structure matrix that includes all information about the structure.

The  $C$  and  $D$  matrices are diagonal and their elements  $C_{RL}$  and  $D_{RL}$  depend on the type of atoms and the orbital numbers  $L = l, m$  ( $l = s, p, d \dots$ ). The values of the potential parameters for the pure metals are calculated by the LMTO method by Andersen et al. [19]. The electronic properties of the disordered alloys are determined by the configurationally averaged one electron Green function. For

the Hamiltonian (1) the Green function is defined as [17]:

$$G_{RL,R'L'}(z) = (z\hat{I} - H)_{RL,R'L'}^{-1} = D_{RL}^{1/2}[P(z) - S]_{RL,R'L'}^{-1}D_{R'L'}^{1/2}, \quad (2)$$

where  $\hat{I}$  denotes the unit operator,  $z$  is the complex energy and the diagonal matrix  $P(z) = (z - C)/D$  is the potential function.

The configurationally averaged Green function  $G_{RL,R'L'}$  can be written as [16, 17]:

$$\langle G(z) \rangle_{RL,R'L'} = A_L(z)\delta_{RR'}\delta_{LL'} + M_L(z)\langle g(z) \rangle_{RL,R'L'}M_L(z) \quad (3)$$

with

$$\langle g(z) \rangle_{RL,R'L'} = \{[P(z) - S]^{-1}\}_{RL,R'L'}. \quad (4)$$

The matrices  $A$  and  $M$  are defined by the potential parameters  $C$  and  $D$  and the potential function  $P$  (for details and notation see [17]).

The coherent potential function  $\mathcal{P}(z)$  is a diagonal matrix for the cubic lattice and its value is determined by the CPA equations [17]:

$$\mathcal{P}(z) = \sum_Q x^Q P_L^Q(z) + [P_L^A(z) - \mathcal{P}_L(z)] \Phi_L(z) [P_L^B - \mathcal{P}_L(z)] \quad (5)$$

with

$$\Phi_L(z) = \frac{1}{N} \sum_k \{[P(z) - S(k)]^{-1}\}_{LL}, \quad (6a)$$

$$P_L^Q(z) = (z - C_L^Q)/D_L^Q. \quad (6b)$$

$S(k)$  is the Bloch transform of the screened structure matrix  $S_{RL,R'L'}$ .

The effect of the disorder can be observed in the Bloch spectral density  $A(k, E)$  defined as [16, 17]:

$$A(k, E) = -\frac{1}{\pi} \text{Im} \sum_L \langle G(k, E + i0) \rangle_{LL}, \quad (7)$$

where  $G(k, E)$  is the Bloch transform of  $G(E)_{RL,R'L'}$ .

In the disordered system we observe the shift and broadening of the peaks in the spectral density  $A(k, E)$ .

The coherent potential approximation gives the simple expression for the partial density of states (PDOS). According to Kudrnovský et al. [16, 17] the PDOS is given by

$$N_L^Q(E) = -\frac{1}{\pi} P_L^Q(E) \text{Im} [P_L^Q(E) - \Omega_L(E + i0)]^{-1}, \quad (8)$$

here

$$\Omega_L(z) = \mathcal{P}_L(z) - [\Phi_L(z)]^{-1}. \quad (9)$$

The total DOS is defined as

$$N(E) = \sum_Q \sum_L x^Q N_L^Q(E) \quad (10)$$

and the Fermi energy  $E_F$  is determined from the condition

$$\int_{-\infty}^{E_F} N(E) dE = \sum_Q x^Q Z^Q, \quad (11)$$

where  $Z^Q$  is the number of valence electrons for  $Q$  compound.

### 3. The electronic density of states for the paramagnetic $Pt_{1-x}Mn_x$ and $Pt_{1-x}Cr_x$ disordered alloys

We consider the  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  paramagnetic disordered alloys for  $0 < x < 0.35$ , i.e. in the region of the concentration where the systems have the fcc-type structure. The calculation of electronic density of states was carried out using the TB LMTO-CPA method. We included the  $s$ -,  $p$ - and  $d$ -states of Pt, Mn and Cr. The  $k$ -summation in (6) was performed for 280  $k$ -points in the irreducible wedge of the Brillouin zone for the fcc structure. The step in energy and its imaginary part was taken as 0.01 Ry. The values of the potential parameters  $C$  and  $D$  in (1) were assumed according to LMTO self-consistent band calculations for the pure metals [19], therefore in this calculation of the density of states we observed the charge transfer from Mn, Cr bands to Pt bands. In the calculation of the screened structure matrices  $S$  we included the first and second nearest neighbours. In Fig. 1 we present the paramagnetic total electronic density of states for the  $Pt_{1-x}Mn_x$  (a) and  $Pt_{1-x}Cr_x$  (b) alloys, respectively.

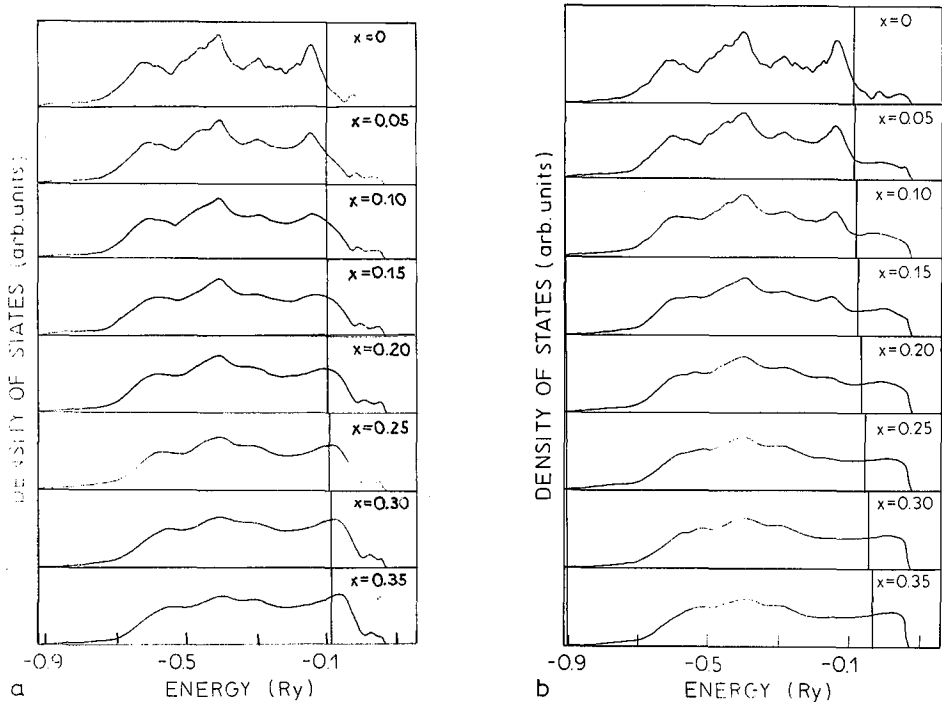


Fig. 1. Total density of states for paramagnetic disordered alloy. Vertical line denotes the Fermi level. (a)  $Pt_{1-x}Mn_x$ , (b)  $Pt_{1-x}Cr_x$ .

The Fermi level is marked by the vertical line. In both systems the shape of the DOS is strongly modified near the Fermi level when the concentration of Mn and Cr increases. We observe the broadening of the peak near  $E_F$ . In pure Pt the

Fermi energy is located on the right side of peak. With the increase in concentration the Fermi level slowly moves towards the lower energy and its position changes to the left side of peak. The first peak in the total DOS is connected with Pt atom, however the second one is due to Mn or Cr atom.

The dependence of  $N(E_F)$  in units (states/Ry atom) on the concentration  $x$  is plotted in Fig. 2a for Pt-Mn and in Fig. 2b for Pt-Cr system. In both cases

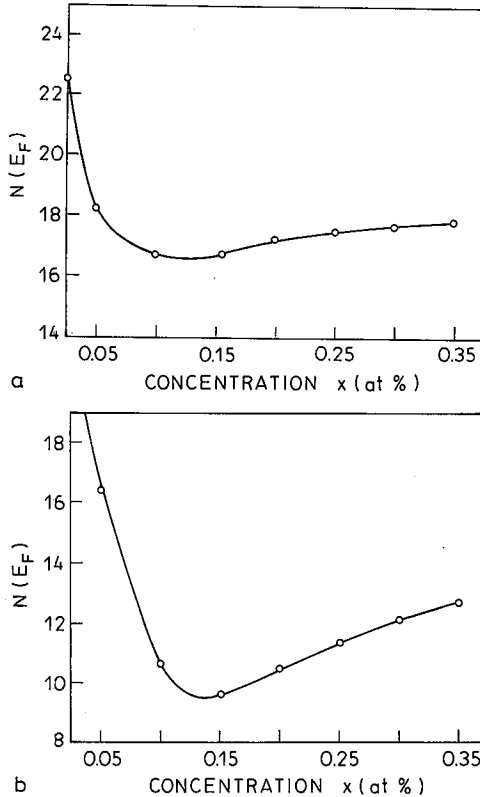


Fig. 2. Dependence of the density of states at the Fermi energy  $N(E_F)$  (states/Ry atom) for (a)  $Pt_{1-x}Mn_x$ , (b)  $Pt_{1-x}Cr_x$ .

the general trend is similar. For  $0 < x < 0.1$  we observed the decrease in  $N(E_F)$  with the increase in  $x$ . Then the value of density of states at the Fermi level slowly increases. From the analysis of the partial density of states for Cr and Pt atom in Pt-Cr alloy and the PDOS for Mn and Pt atom in Pt-Mn alloy we found that the contribution from the  $s$ - and  $p$ -bands to the DOS at the Fermi level is very small and the main contribution comes from the  $d$ -band of Mn, Cr and Pt atoms.

In ordered alloys the Bloch spectral density  $A(k, E)$  (Eq. (7)) would be a set of infinitely sharp peaks where  $E$  is an allowed energy for a given  $k$ . In disordered Pt-Mn and Pt-Cr alloys we observe the shift and broadening of peaks in the Bloch spectral densities with increasing concentration. This fact indicates the strong disorder in these alloys. In Fig. 3a and 3b we plotted the dependence of

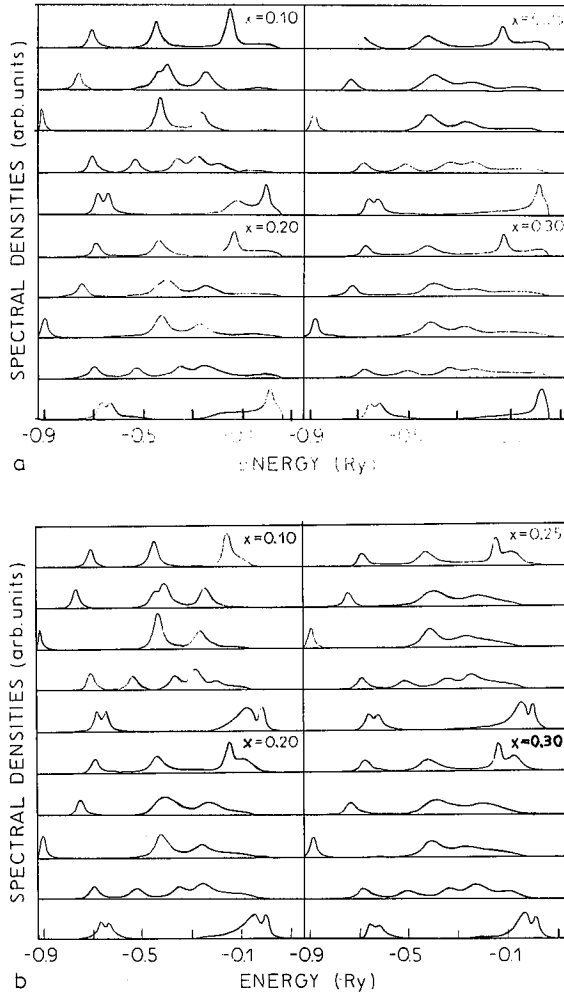


Fig. 3. The Bloch spectral density function  $A(k, E)$  in (a)  $Pt_{1-x}Mn_x$  and (b)  $Pt_{1-x}Cr_x$ . The points in the fcc Brillouin zone are as follows (from top to bottom for each concentration) — points  $L$  : (0.5, 0.5, 0.5),  $\Gamma$  : (0.25, 0.25, 0.25) and (0, 0, 0),  $X$  : (0.5, 0.0) and (1, 0, 0).

$A(k, E)$  on energy for  $Pt_{1-x}Mn_x$  (a) and  $Pt_{1-x}Cr_x$  (b) for points  $X$  — (1, 0, 0) and (0.5, 0, 0),  $\Gamma$  — (0, 0, 0) and (0.25, 0.25, 0.25),  $L$  — (0.5, 0.5, 0.5).

**4. Magnetic stability in  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  disordered alloys**

We study the magnetic properties of the disordered  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  for  $0 < x < 0.35$  in terms of the modern formulation of the Stoner model of magnetism [25, 26]. From the total energy band theory Marcus and Moruzzi [25] obtained the generalized Stoner condition for the occurrence of ferromagnetism.

The Stoner model gives the change of the total energy  $\Delta E_T$  of the crystal when the magnetic moment changes from zero to  $m$ . According to Marcus and Moruzzi [25] we can write

$$E_T(m, V) = 0.5 \int_0^m \frac{\bar{m}d\bar{m}}{N(\bar{m}, V)} - 0.25Im^2, \quad (12)$$

where  $N(m, V)$  is the averaged density of states defined over energy intervals around the Fermi energy  $E_F$  containing  $m/2$  electrons above and below  $E_F$ :

$$N(m, V) = m/[E(m, V) - E(-m, V)]. \quad (13)$$

Here  $E(m, V)$  denotes the Fermi energy  $E_{F\sigma}$  for spin  $\sigma$  and its value is determined by the condition

$$\int_{E_F}^{E(m, V)} N(x, V)dx = m/2, \quad (14)$$

where  $N(E, V)$  is the paramagnetic DOS calculated for the given volume of crystal.

TABLE  
The generalized Stoner parameter  $I$  in disordered  
 $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  alloys.

| $x$  | $Pt_{1-x}Mn_x$        |           | $Pt_{1-x}Cr_x$        |           |
|------|-----------------------|-----------|-----------------------|-----------|
|      | $I$ [Ry]<br>min.-max. | $N(E_F)I$ | $I$ [Ry]<br>min.-max. | $N(E_F)I$ |
| 0.05 | 0.053-0.071           | 0.96-1.29 | 0.061-0.093           | 0.99-1.53 |
| 0.10 | 0.058-0.064           | 0.97-1.07 | 0.092-0.095           | 0.97-1.00 |
| 0.15 | 0.059-0.062           | 0.99-1.04 | 0.091-0.100           | 0.87-0.96 |
| 0.20 | 0.060-0.061           | 1.03-1.05 | 0.089-0.095           | 0.93-0.99 |
| 0.25 | 0.060-0.061           | 1.05-1.06 | 0.086-0.088           | 0.98-1.00 |
| 0.30 | 0.060                 | 1.06      | 0.082-0.083           | 0.99-1.00 |
| 0.35 | 0.060                 | 1.07      | 0.079                 | 0.99      |

From the minimum of the total energy  $\Delta E_T$  with respect to  $m$ , we get the Stoner criterion for the stable magnetic moment in the system for the given  $m$ :

$$N(m, V) \cdot I = 1, \quad (15)$$

where  $I$  is the generalized Stoner parameter for alloys [27, 28]. Jaswal [27] postulated the approximate form of  $I$  in the case of binary alloys

$$I = \sum_Q I_Q [N_Q(E_F)/N(E_F)]^2. \quad (16)$$

Here  $I_Q$  is the local-spin-density (LSD) Stoner parameter [29, 30] for the given atom,  $Q$  and  $N_Q(E)$  is the partial density of states for  $Q$ -atom.

From Eq. (15) we can estimate the values of the generalized Stoner parameter  $I$  for a given concentration. In Fig. 4 we plotted the dependence of  $N(m, V)$  on

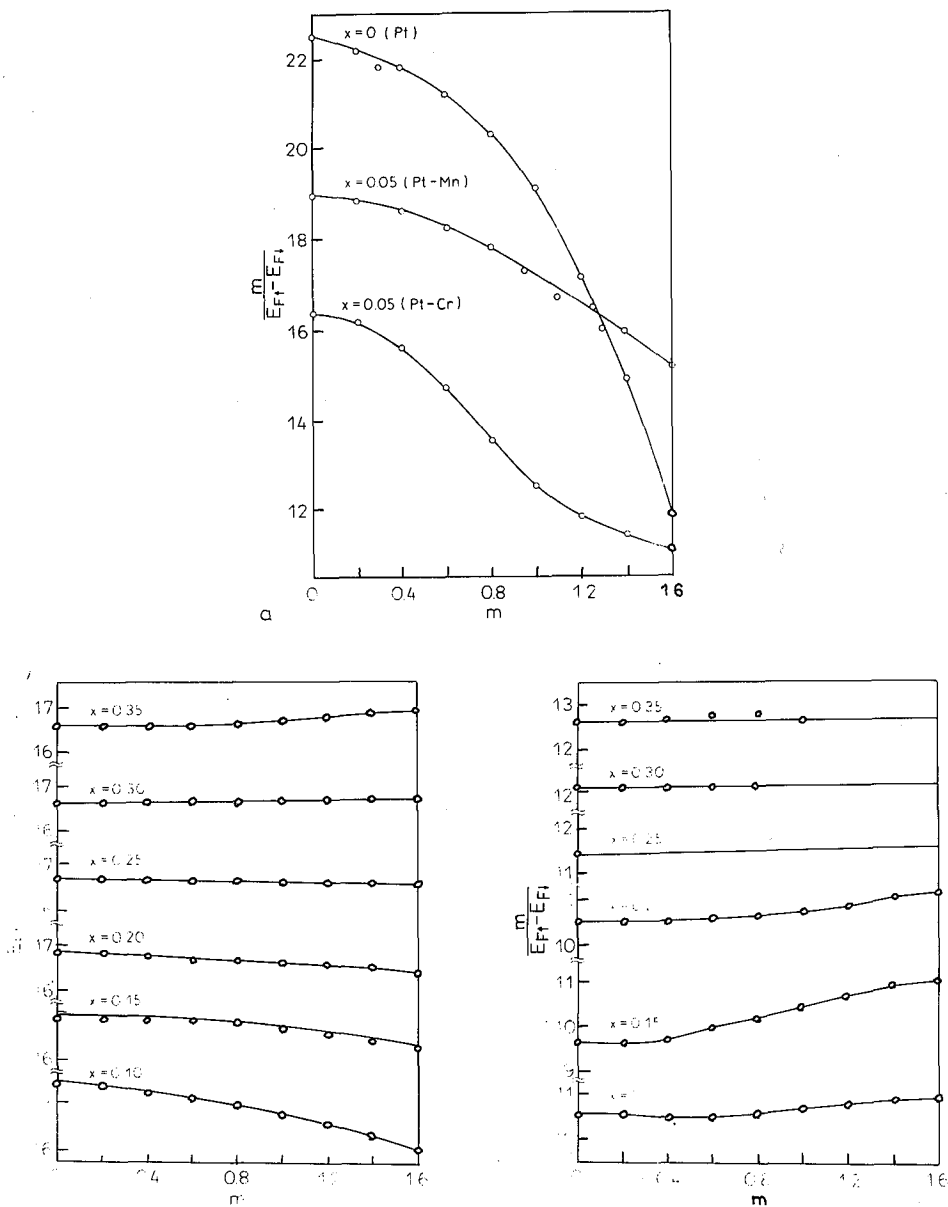


Fig. 4. The dependence of average density  $N(m) = m / (E_{F\uparrow} - E_{F\downarrow})$  on the magnetic moment  $m$ : (a) for Pt-Mn(Cr)  $x = 0.05$ , (b) for  $Pt_{1-x}Mn_x$ , (c) for  $Pt_{1-x}Cr_x$  ( $0.10 < x < 0.35$ ).

the magnetic moment for various concentrations of Mn and Cr. For  $x > 0.2$  the values of  $N(m, V)$  change very slowly with the increase in the magnetic moment. In Table we present the values of the Stoner parameter  $I$  for  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$



alloys. The values of  $N(E_F)I$  are less than 1 or little greater than 1 (in the case of  $Pt_{1-x}Mn_x$  alloy). This fact indicates that the disordered  $Pt_{1-x}Mn_x$  and  $Pt_{1-x}Cr_x$  alloys are paramagnetics or very weak ferromagnetics in the range of concentration  $0.05 < x < 0.35$  at.% Mn or Cr. For  $x = 0.05$  at.% Mn(Cr) we find the solution of Eq. (15) for the small magnetic moment  $m = 0.05 \mu_B$ . The values of the generalized Stoner parameter  $I$  estimated by Eq. (16) or using the simple form  $I = \sum_Q x^Q I^Q$  for  $I^Q$  taken from [29, 30] are smaller than the values obtained directly from Eq. (15).

## 5. Conclusions

The measurements of the electronic and magnetic properties of Pt-Mn and Pt-Cr compounds [1-3,7] showed the significant role of the distribution of atoms in the fcc structure. Our results of the calculation based on TB LMTO-CPA method confirm partially the experimental observation. We found that the values of the electronic density of states at the Fermi level  $N(E_F)$  in disordered Pt-Mn and Pt-Cr alloys are small and the Stoner criterion is not satisfied. The preliminary calculations of the electronic structure for the partially ordered systems indicate that the value of  $N(E_F)$  increases with the increase in chemical ordering in the lattice. The examination of the electronic structure of disordered paramagnetic Pt-Mn and Pt-Cr compounds is the first step in understanding of the electronic and magnetic properties of these compounds.

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