

The electronic structure and magnetism of MoPd_3 and MnPd_3

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

1989 J. Phys.: Condens. Matter 1 2211

(<http://iopscience.iop.org/0953-8984/1/12/005>)

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 18:02

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

The electronic structure and magnetism of MoPd₃ and MnPd₃

Tashi Nautiyal and Sushil Auluck

Physics Department, University of Roorkee, Roorkee-247667, India

Received 27 July 1988, in final form 16 November 1988

Abstract. We have calculated the self-consistent band structure of paramagnetic MoPd₃ and MnPd₃ by using the linear-muffin-tin-orbital method. The results for the density of states at equilibrium, lattice constant, the variation in pressure with volume and the bulk modulus are reported here. Also, the possibility of magnetic ordering in these compounds has been explored. Comparisons are made with recent theoretical and experimental results.

Recently, Jaswal (1984) has studied the possibility of magnetic order in MoPd₃ and MnPd₃ which are transition-metal compounds with non-magnetic constituents. He used the orthogonalised linear combination of atomic orbitals (OLCAO) and applied the Stoner criterion. Since Jaswal's calculations were done using a non-self-consistent band structure, his conclusions could be influenced by the choice of the potential. It would therefore be meaningful to determine how self-consistent band calculations affect the conclusions. With this in mind, we have performed self-consistent band calculations using the linear-muffin-tin-orbital (LMTO) method (Andersen 1975, Skriver 1984). In this paper, we report the results of such calculations and compare our results with those of Jaswal.

The LMTO method in the atomic-sphere approximation with combined correction terms has been used. The calculations are semi-relativistic in nature where mass-velocity and Darwin terms are included in the solution of the Dirac equation but with the spin-orbit terms excluded. The exchange potential used for both compounds is the von Barth-Hedin potential. It is assumed that the core states remain unchanged as one goes from the atom to the solid compound—hence atomic core charge densities are used throughout—and that there is no overlap between the core states on different atoms in the solid. Both MoPd₃ and MnPd₃ exist in the cubic Cu₃Au structure and both have a lattice constant equal to 3.89 Å. Within spheres around each atomic centre the wavefunction is expanded in muffin-tin orbitals. The basis set included s, p and d orbitals ($l_{\max} = 2$) for each site. The Wigner-Seitz radius was scaled so that the total volume of all spheres equals that of the unit cell. The spheres around the atoms for the two constituent metals were taken to be of equal size with their radius equal to 2.8732 au. The one-electron potentials were self-consistently obtained by performing self-consistent iterations on a mesh of 84 *k*-points in the irreducible one-fortyeighth part of the Brillouin zone. The calculations were done for the paramagnetic structure of the two compounds.

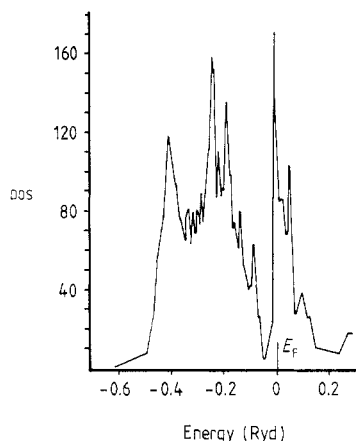


Figure 1. DOS for paramagnetic MoPd₃.

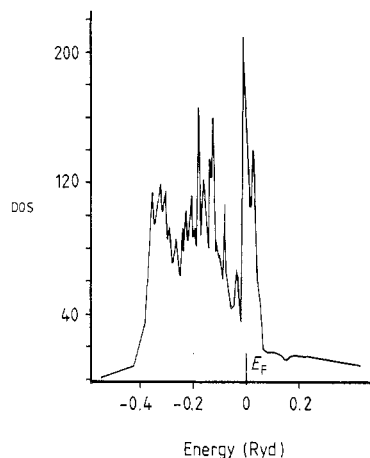


Figure 2. DOS for paramagnetic MnPd₃.

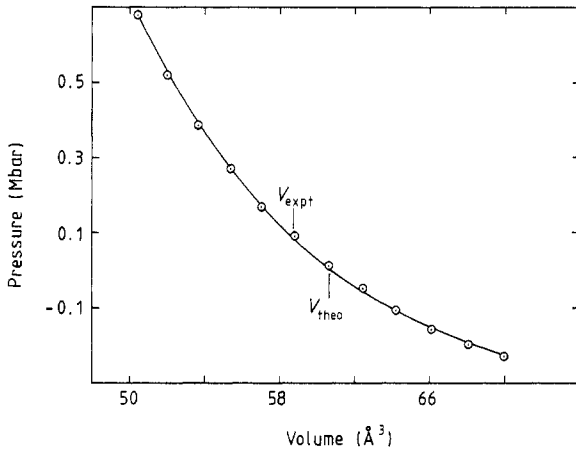
We have determined the total and partial (by atom type and orbital-angular-momentum-decomposed) density of states (DOS) for MoPd₃ and MnPd₃. The DOS for paramagnetic MoPd₃ is shown in figure 1 and that for paramagnetic MnPd₃ in figure 2. The DOS for both compounds have a number of peaky structures. The contribution to the DOS from Pd d states is predominant below the Fermi energy while the DOS around and above the Fermi energy is mainly due to Mo or Mn contribution. As can be seen from the figures, the Fermi energy lies on a relatively narrow peak which arises mainly from the Mo or Mn d states. The DOS $N(E_F)$ at the Fermi energy is nearly 8.88 states eV⁻¹/unit cell for MoPd₃ and 11.34 states eV⁻¹/unit cell for MnPd₃. The $N(E_F)$ values are quite high for both compounds. However, these values have an element of uncertainty because of the sharpness of the peak in the region of the Fermi level. Comparing our results with those of Jaswal, we observe that Jaswal obtains a DOS of 7.1 states eV⁻¹/unit cell for MoPd₃ which is slightly smaller than our value. For MnPd₃, however, he obtains a much smaller value of 8.7 states eV⁻¹/unit cell compared with the DOS that we obtain. This difference in DOS could be due to the non-self-consistent nature of Jaswal's calculations. Using the relationship between the coefficient of linear specific heat and the DOS at the Fermi energy $\gamma = (\pi^2/3)k_B^2 n(E_F)(1 + \lambda)$ and assuming λ , the mass enhancement factor, which is not known for these systems, to be zero, we obtain $\gamma = 21.07$ mJ mol⁻¹ K⁻² for MoPd₃ and $\gamma = 27.06$ mJ mol⁻¹ K⁻² for MnPd₃. Because of lack of experimental data for γ of these compounds, we are unable to make any comparisons. All we can say is that these values of γ are an underestimate since, in practice, $\lambda > 0$.

The projected DOS $N_l^t(E_F)$ for different orbitals l at different sites t of the compounds, the site DOS $N^t(E_F)$ and the total DOS $N(E_F)$ at the Fermi level for the two compounds are listed in table 1. We do not know of any experimental estimates to compare our results with. Most of the contribution to $N(E_F)$ comes from the d states of the constituent metals. The Fermi energy turns out to be 0.71 Ryd for MoPd₃ and 0.59 Ryd for MnPd₃. The pressure (Skriver 1984) at the experimental lattice constant is 0.09 Mbar for MoPd₃ and -0.10 Mbar for MnPd₃. We find that a total of 0.21 electrons/atom are transferred to Mo from the three Pd atoms in MoPd₃. In MnPd₃, a relatively smaller charge transfer, 0.02 electrons/atom, to the Mn atom takes place.

In our earlier work (Auluck and Nautiyal 1989) on VPt₃, we calculated the PV curve self-consistently at each volume. We also applied the scaling procedure for the same

Table 1. Projected DOS at the Fermi level for MoPd_3 and MnPd_3 .

Compound	Site	$N_i^l(E_F)$ (states $\text{eV}^{-1}/\text{unit cell}$)			$N(E_F)$ (states $\text{eV}^{-1}/\text{unit cell}$)	$N(E_F)$ (states $\text{eV}^{-1}/\text{unit cell}$)
		s	p	d		
MoPd_3	Mo	0.01	0.09	5.44	5.54	8.88
MoPd_3	Pd	0.09	0.48	2.77	3.34	
MnPd_3	Mn	0.03	0.08	7.65	7.75	11.34
MnPd_3	Pd	0.05	0.20	3.33	3.59	

**Figure 3.** Pressure against volume for MoPd_3 .

where, starting with the self-consistent results for the equilibrium volume, we scaled our results to obtain pressure at other volumes (using Skriver's LMTO code). It was found that the values of pressure derived by the scaling procedure were only slightly different from those obtained self-consistently at every volume. In the light of these calculations, we feel that the scaling procedure is accurate for the calculation of pressure at various volumes. In figures 3 and 4, we have shown variation in pressure as a function of volume, using the scaling procedure, for these compounds.

The theoretically determined equilibrium lattice constant, at the point where the pressure is zero, as shown in the figure, turns out to be 3.94 \AA in MoPd_3 and is larger than the experimental lattice constant by 1.2%. The theoretical equilibrium lattice constant of 3.84 \AA for MnPd_3 is smaller than the experimental lattice constant by 1.2%. The bulk modulus $B = -V dP/dV$ as determined from these curves is $2.35 \times 10^{11} \text{ N m}^{-2}$ for MoPd_3 and $1.68 \times 10^{11} \text{ N m}^{-2}$ for MnPd_3 . These values together with those for the constituent metals (Kittel 1985) Mo, Pd and Mn are listed in table 2. We observe that the bulk modulus of the compounds lies between those of their constituent metals.

Next we try to see whether magnetic ordering is predicted in these two compounds which have non-magnetic constituent metals. The Stoner criterion for magnetism in compounds is given by Jarlborg and Freeman (1980) as $IN(E_F) > 1$ where I is Stoner-like parameter given by

$$I = \frac{1}{12\pi} \int_0^{R_{ws}} r^2 \mu(\rho) \delta(\rho) \frac{R_{t1}^4(E_F, r)}{\rho(r)} dr$$

when the t_1 band dominates the DOS at E_F . Here $R_{t1}(E_F, r)$ is the radial wavefunction

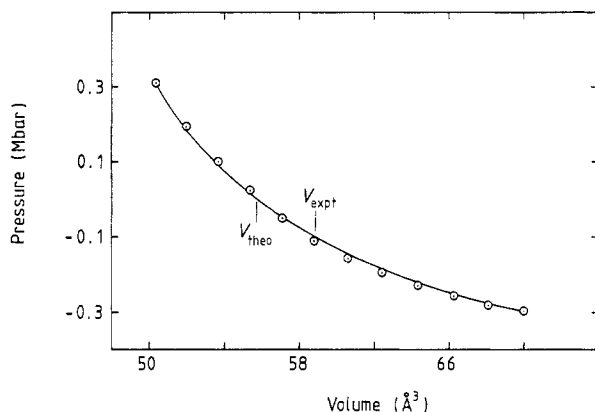


Figure 4. Pressure against volume for MnPd_3 .

Table 2. Bulk modulus B .

Constituent	B (10^{11} N m^{-2})	Compound	B (10^{11} N m^{-2})
Mo	2.725	MoPd_3	2.352
Pd	1.808	MnPd_3	1.681
Mn	0.596		

normalised to the Wigner–Seitz sphere at site t . μ is the Kohn–Sham potential and is expressed in the electron parameter r_s , as

$$\delta(\rho) = 1 - 0.036r_s - 1.36r_s/(1 + 10r_s)$$

with $4\pi r_s^3 = 1/\rho(r)$. Simplifying this criterion, one obtains (Jaswal 1984)

$$I \approx \sum_t I_t \left(\frac{N^t(E_F)}{N(E_F)} \right)^2$$

where I_t is the Stoner parameter for the d orbitals, which dominate the DOS at E_F , at site t . Using the values of I from the work of Janak (1977), we obtain $IN(E_F)$ as 1.14 for MoPd_3 , implying magnetic ordering in this compound. Jaswal, however, obtains $IN(E_F) = 0.64$ for this compound, hence predicting it to be a non-magnetic compound. Experimental results for the ordered MoPd_3 are not available. The contrast in the two theoretical results could be due to the non-self-consistent nature of Jaswal's calculations. Also the Fermi level lying on a sharp peak in our DOS as well as in Jaswal's DOS emphasises the need to locate it accurately since even a small shift in the Fermi level would affect the DOS drastically. Since our value of $IN(E_F)$ for MoPd_3 is quite close to unity, we tried to ascertain the accuracy of our DOS at the Fermi level. For this,

- (i) we extended the basis set to include the f ($l = 3$) states of Mo and Pd and
- (ii) took a finer mesh of 165 k -points.

Both the methods, however, gave $IN(E_F)$ greater than unity (1.21 and 1.28, respectively), verifying our prediction of magnetic ordering as made above. For MnPd_3 , we find that $IN(E_F)$ equals 2.22, i.e. greater than unity, in agreement with the value of

1.4 obtained by Jaswal. This compound is thus expected to be magnetic in nature. Experimentally (Cable *et al* 1962), MnPd_3 is known to order antiferromagnetically below 170 K.

To sum up, we have studied the electronic structure of paramagnetic MoPd_3 and paramagnetic MnPd_3 . Our calculations predict a small charge transfer from the three Pd atoms to Mo and Mn atoms. We have studied the variation in pressure with volume. Theoretical values of the lattice constant for the two compounds are within 1.2% of the experimental lattice constant. The bulk moduli for the two compounds lie between those of the constituent metals. If we apply the Stoner criterion for compounds, both the compounds are predicted to have magnetic ordering. Experimentally MnPd_3 is known to order antiferromagnetically while results for ordered MoPd_3 are not available.

Acknowledgments

One of us (SA) is grateful to the North Dakota State University for a visiting professorship during which some of these calculations were done on the IBM 3081 computer. Financial assistance from the CSIR, India, is gratefully acknowledged.

References

- Andersen O K 1975 *Phys. Rev. B* **12** 3060
Auluck S and Nautiyal T 1989 *Phys. Rev. B* submitted
Cable J W, Wollan E O, Koehlar W C and Child H R 1962 *Phys. Rev.* **128** 2118
Janak J F 1977 *Phys. Rev. B* **16** 255
Jarlborg T and Freeman A J 1980 *Phys. Rev. B* **22** 2332
Jaswal S S 1984 *Solid State Commun.* **52** 127
Kittel C 1985 *Introduction to Solid State Physics* (New Delhi: Wiley Eastern)
Skriver H L 1984 *Springer Series in Solid State Sciences* vol 41, ed. M Cardona and P Fulde (Berlin: Springer)