PHYSICAL REVIEW B VOLUME 39, NUMBER 12 15 APRIL 1989-II

Electronic structure and magnetism in VPt_3

S. Auluck and T. Nautiyal
Physics Department, University of Roorkee, Roorkee-247 667, India

(Received 19 August 1988)

The electronic and magnetic states in VPt_3 have been investigated by self-consistent band-structure calculations using the linear-muffin-tin-orbitals method. The calculations are performed in both the paramagnetic and spin-polarized configurations for the metastable cubic, as well as the stable tetragonal crystal structure. The results are compared with experiment and other theoretical calculations.

INTRODUCTION

In our previous paper,[1] we presented calculations on the nonmagnetic transition-metal alloy VPd_3, which has nonmagnetic constituents, in two different structures. For the $TiAl_3$ structure we obtain good agreement with experiment, while for the hypothetical Cu_3Au structure our calculations were in agreement with earlier calculations.

In the present paper, we study the compound VPt_3, which again has nonmagnetic transition-metal constituents. Turek *et al.*[2] found that the whole V-Pt system is non-magnetic except for the ordered VPt_3, which is ferromagnetic. It can be synthesized in either the Cu_3Au or the $TiAl_3$ structure. Interestingly, in both the structures it is reported[3] to have the same small saturation magnetic moment of $0.1\mu_B$. We report calculations on the paramagnetic and the spin-polarized configurations of VPt_3 in the $TiAl_3$ structure as well as the Cu_3Au structure. The unit cell in the former (latter) consists of 8 (4) atoms. The self-consistent band structure was calculated using the linear muffin-tin-orbitals (LMTO) method[4] including the combined correction terms in the atomic-sphere approximation. The calculations were carried out using the values for the lattice constant $a = 3.87$ Å and a c/a ratio of 2.027, which is close to the ideal value of 2.0. The volume per formula unit is 58.74 Å^3 or 396.82 a.u.[3] at the equilibrium lattice constant. The wave function is expanded in muffin-tin orbitals within spheres around each atomic center. We use muffin-tin orbitals with angular momentum $s-d$ on both the V and the Pt spheres. For simplicity, we chose the ratio of the Wigner-Seitz radii of V and Pt to be unity. A mesh of 75 **k** points in the irreducible $\frac{1}{16}$ of the centered tetragonal Brillouin zone (BZ) was used for the $TiAl_3$ structure and one of 84 **k** points in the irreducible $\frac{1}{48}$ of the BZ for the Cu_3Au structure.

RESULTS

$TiAl_3$ structure

The density of states (DOS) for the paramagnetic VPt_3 is shown in Fig. 1. An angular momentum decomposition of the DOS shows that below the Fermi energy (E_F), the contribution from platinum d states is predominant. The E_F does not lie on a sharp peak. The projected DOS at the E_F for different orbitals (l) of the two constituents is listed in Table I. The DOS at the E_F, $N(E_F)$, is 3.74 states/eV unit-cell. The spin-polarized DOS is shown in Fig. 2. The DOS for majority and minority bands is almost the same and the structure of the DOS does not show any significant change in going from the unpolarized to the spin-polarized state. Perhaps this in itself is an indication of a very small magnetic moment for this compound. The value of the converged magnetic moment is $0.410\mu_B$, which is somewhat higher than the experimental value[3] of $0.1\mu_B$. Kubler[5] using the augmented-spherical-wave (ASW) method found the magnetic moment nearly equal to zero for VPt_3 in $TiAl_3$ structure predicting it to be nonmagnetic. A small amount of charge transfer ($0.057e$) from V to the three Pt atoms is predicted by our calculations.

For spin-polarized calculations, we have calculated the magnetic moment and pressure as a function of the lattice constant a using a coarse mesh of 30 **k** points in the irredicible BZ. Calculations were done self-consistently for every value of lattice constant. The magnetic mo-

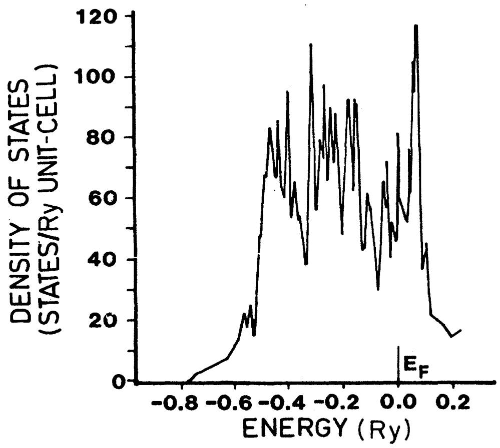

FIG. 1. The density of states for paramagnetic VPt_3 in $TiAl_3$ crystal structure. The energy zero is at the Fermi energy.

TABLE I. Projected density of states (states/eV cell) at the Fermi level for VPt_3.

Ordered struct. type	Site	s	p	d	$N(E_F)$
$TiAl_3$	V	0.01	0.04	1.76	3.74
	Pt	0.03	0.17	1.73	
Cu_3Au	V	0.02	0.06	7.38	
	Pt	0.03	0.27	2.46	

ment, as shown in the upper panel of Fig. 3, is seen to rise with increase in a. The rate of increase is slightly larger beyond $a = 3.96$ Å. Shown in the lower panel of Fig. 3 is the variation of pressure with lattice constant. The theoretically determined equilibrium lattice constant, at the point where the pressure is zero, as shown in the figure, and the experimental lattice constant differ by 2.0%.

The low-temperature specific-heat measurements give the value of the linear coefficient of specific heat γ equal to 3.24 $mJ/mol\,K^2$ for the ordered compound in the $TiAl_3$ configuration.[6] Assuming the electron-phonon mass enhancement factor λ, which is not known for this system, to be zero, the DOS at the Fermi level as derived from the experimental value of γ is 1.36 states/eV unit-cell. Our calculated value of 3.74 states/eV unit-cell is too high. Kubler[5] gets the DOS at Fermi level equal to 3.6 states/eV unit-cell for the $TiAl_3$ structure, which is very close to our calculations.

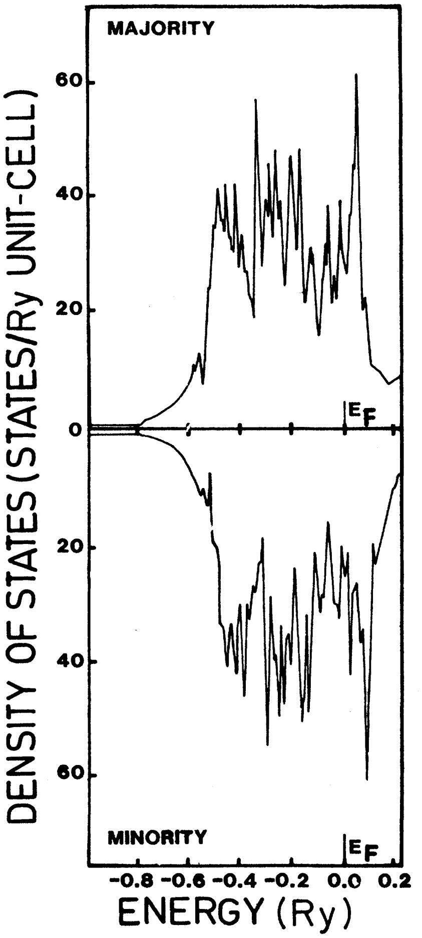

FIG. 2. The total density of states for spin-polarized VPt_3 in $TiAl_3$ crystal structure.

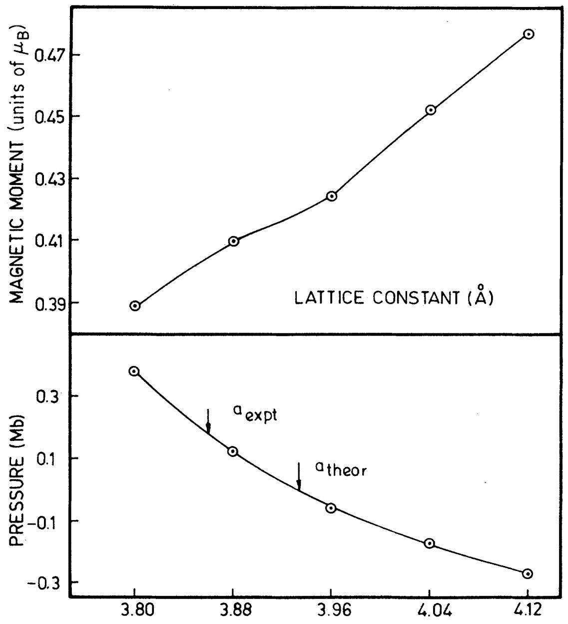

FIG. 3. Magnetic moment (upper panel) and pressure (lower panel) as a function of lattice constant a for spin-polarized VPt_3 in $TiAl_3$ structure.

Cu_3Au structure

The difference in the results for the Cu_3Au structure is quite remarkable, as is also the case for VPd_3.[1,5] The DOS is shown in Fig. 4 for the paramagnetic VPt_3. In

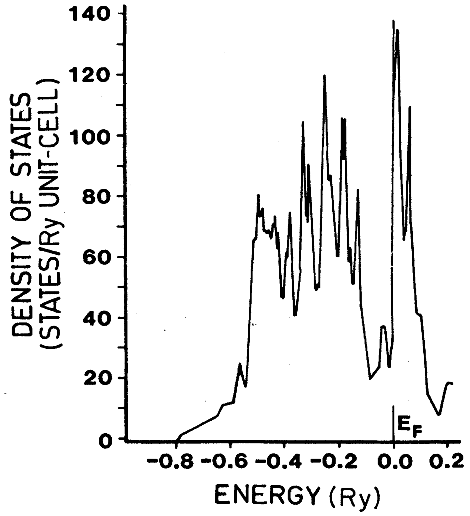

FIG. 4. The density of states for paramagnetic VPt_3 in the Cu_3Au structure.

this case the E_F lies in a sharp peak, in contrast to the $TiAl_3$ structure. Below E_F, the DOS is composed basically of platinum d states. The sharp, narow peak at E_F is due to the vanadium d states. The demarcation between the vanadium d peak and platinum d states is very clear in this case. The value of the DOS at E_F is as high as 10.22 states/eV unit-cell. The projected DOS for different orbitals is shown in Table I. The spin-polarized DOS is shown in Fig. 5. A charge equal to $0.0213e$ is found to transfer from the vanadium atom to the three platinum atoms. The value of the converged magnetic moment in this case is $1.30\mu_B$, which is very high as compared to the experimental value, but is in agreement with the calculations of Kubler,[5] who obtains a value of $1.3\mu_B$. Theoretical results thus imply that atomic ordering can drastically modify the physical properties of an alloy, as for example going from the $TiAl_3$ structure to the Cu_3Au structure. To bridge this gap between theory and experiment, we feel some more experiments must be performed on the metastable Cu_3Au configuration of VPt_3.

The variation of magnetic moment(pressure) with a is shown in the upper (lower) panel of Fig. 6. Once again the results are self-consistent for every value of a and a coarse mesh of 35 **k** points is used in the irreducible BZ. The magnetic moment rises steadily with increase in a showing a sharper rise for a around 4.060 Å. Although the variation of magnetic moment with a is similar for the $TiAl_3$ and the Cu_3Au structures, the magnitude of the magnetic moment in the Cu_3Au structure is very high as compared to that in the $TiAl_3$ structure. The theoretically determined equilibrium lattice constant, marked in the lower curve, is within 1.9% of the experimental lattice constant.

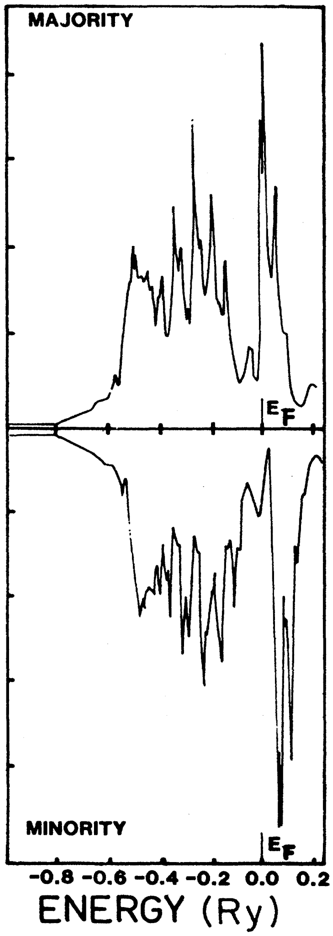

FIG. 5. The total density of states for spin-polarized VPt_3 in Cu_3Au crystal structure.

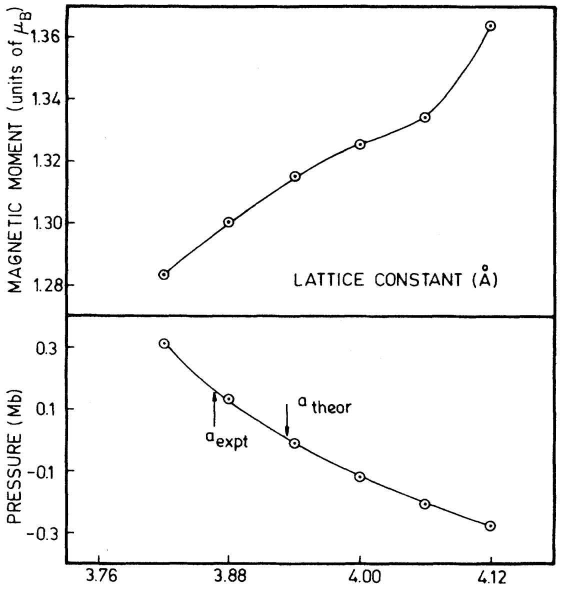

FIG. 6. Magnetic moment (upper panel) and pressure (lower panel) as a function of cubic lattice constant for spin-polarized VPt_3 in Cu_3Au crystal structure.

In the course of the calculations we found that although the use of the LMTO scaling principle greatly reduces the number of iterations needed to obtain a self-consistent solution, it will in general not give the correct magnetic moment unless one is already very close to self-consistency. Hence for magnetic compounds one must include several band calculations in the self-consistency cycle at each lattice spacing. The pressure–lattice-constant variation, however, shows the same trend in both the Cu_3Au and $TiAl_3$ structures whether the calculations are done self-consistently or by using the scaling principle.

The experimental value of the linear coefficient of specific heat for VPt_3 in the ordered Cu_3Au configuration is 3.00 mJ/mol K^2. Once again assuming the λ to be zero, for lack of experimental data, this gives a DOS of 1.26 states/eV unit-cell at E_F, which is very small compared to our theoretical value or to Kubler's calculations (4.3 states/eV unit-cell).

DISCUSSION AND CONCLUSIONS

We observe that the electronic structure of a compound, and hence its physical properties, are determined to a great extent by its crystal structure. In the stable $TiAl_3$ configuration our theoretical results are quite close to the experimental results. However, in the metastable Cu_3Au configuration of VPt_3 we obtain a magnetic moment equal to $1.30\mu_B$, which is very high compared to the experimental value. Also, the DOS at E_F in the Cu_3Au configuration is much larger than the experimental value. A comparison of our results for VPt_3 with our earlier calculations for VPd_3 does not show any significant changes when Pd is replaced by Pt. Our results are qualitatively in agreement with the ASW calculations of Kubler. The potential in our calculations is spherically symmetric. The anisotropy in the potential, by inclusion of nonspherical components, might broaden the vanadium *d* states. This in turn may lower the DOS at E_F and the magnetic moment. However, the wide gap between theory and experiment in the metastable Cu_3Au configuration is less likely to be bridged by an anisotropic potential alone. More experiments for the metastable Cu_3Au configuration of VPt_3 are welcomed to find a definite answer and solution to the problem.

ACKNOWLEDGMENTS

We would like to thank Professor B. N. Harmon for introducing us to the LMTO method, and Dr. H. L. Skriver, for sending us the LMTO codes. Part of this work was done when one of us (S.A.) was visiting the North Dakota State University (Fargo, ND). We would like to thank the Computer Center of North Dakota State University for allowing us the use of their IBM 3081 computer.

---

[1] D. K. Misemer, S. Auluck, D. J. Sellmyer, S. S. Jaswal, and A. J. Arko, Phys. Rev. B **31**, 3356 (1985).

[2] P. Turek and R. Kuentzler, Physica B+C **107B**, 257 (1981).

[3] R. Jesser, A. Bieber, and R. Kuentzler, J. Phys. (Paris) **42**, 1157 (1981).

[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); H. L. Skriver, in *The LMTO Method,* Vol. 41 of *Solid State Sciences,* edited by M. Cardona and P. Fulde (Springer-Verlag, New York, 1984).

[5] J. Kübler, J. Magn. Magn. Mater. **45**, 415 (1984).

[6] P. Turek, R. Kuentzler, A. Bieber, and R. Jesser, Solid State Commun. **53**, 979 (1985).