Photoemission, electronic structure, and magnetism in VPd$_3$

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Electronic and magnetic states in the ordered compound VPd$_3$ have been investigated with photoemission measurements and self-consistent band-structure calculations. The linear combination of muffin-tin orbitals method was used to study VPd$_3$ in a hypothetical cubic crystal structure and the actual tetragonal crystal structure, and the calculations were performed for both paramagnetic and spin-polarized configurations. The results for the cubic structure are in agreement with earlier calculations, while the results from the tetragonal structure are in much better agreement with the photoemission and other measurements.

INTRODUCTION

In 1981 Williams *et al.* made a prediction that VPd$_3$, a compound in which the constituents are nonmagnetic, should be ferromagnetic, and calculated the magnetic moment to be $1.4\mu_B$.[1] The prediction was based on the results of local-spin-density functional band-structure calculations assuming the Cu$_3$Au cubic structure for VPd$_3$. The result was particularly interesting since the magnetism arose in part from different spectral weights in the majority- and minority-spin bands and not entirely from a Stoner-Wohlfarth-Edwards mechanism, in which the majority- and minority-spin bands are rigidly shifted. Subsequently, pure samples of the material were prepared and measurements of the magnetic susceptibility were obtained.[2] The measurements showed no evidence of magnetic ordering down to temperatures of 1.6 K.

The calculations of Ref. 1, which resulted in the prediction of covalent magnetism, showed that the Fermi level (E_F) lay in a region of vanadium d states, and that the value of the density of states at the Fermi level was quite high. The Stoner model of magnetism emphasizes the density of states (DOS) at the Fermi level,[3] and a high state density at E_F suggests, but does not guarantee, the formation of a magnetic compound. The magnetic moment resulting from a spin-polarized calculation was, however, much higher than the moment predicted from the Stoner model alone. The additional magnetic moment resulted from the redistribution of the spectral weights of the bands, and this interesting result was termed covalent magnetism.

The resolution of the difference between theory and experiment was suggested in the results of nonself-consistent band-structure calculations of Jaswal,[4] in which he took the actual crystal structure of the material into account. The crystal structure of VPd$_3$ is not cubic Cu$_3$Au structure, but the related centered tetragonal TiAl$_3$ structure.

Both structures (shown in Fig. 1) are based on a fcc lattice, and both structures have the same number and type of atoms in the first coordination shell. In both structures the palladium has 4 nearest-neighbor vanadium atoms and 8 nearest-neighbor palladium atoms. Of even more importance, in view of the results which follow, is that vanadium is surrounded by 12 nearest-neighbor palladium atoms in both structures. In spite of the similarities in the arrangement of atoms, the two crystal types have very different electronic structures. Jaswal found that the Fermi energy lay near a minimum in the density of states, well below the vanadium d-band peak. Indeed the density of states at E_F did not satisfy the Stoner criterion,[5] and he concluded that VPd$_3$ would not be magnetic. There are, however, two difficulties with the non-self-consistent calculation: first, the results depend critically on the choice of potential parameters; second, the type of magnetism
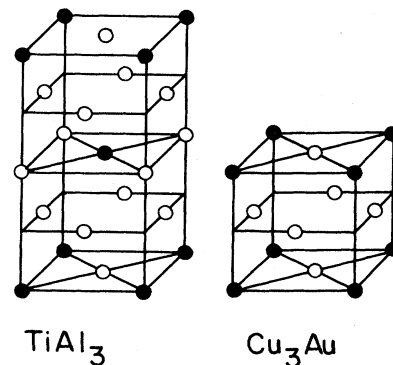

FIG. 1. Unit cells for TiAl$_3$ (tetragonal) and Cu$_3$Au (cubic) crystal structures.

ruled out by the calculation is Stoner magnetism, not the covalent magnetism predicted by Williams *et al.* Both difficulties are overcome by self-consistent, spin-polarized electronic structure calculations in the tetragonal structure.

In this paper we present the results of self-consistent band-structure calculations of VPd$_3$ in the TiAl$_3$ crystal structure for both spin-polarized and paramagnetic configurations. To demonstrate that the structural difference is responsible for the absence of a magnetic state at low temperatures, we have repeated the Cu$_3$Au calculation as well. Since the magnetic ordering depends on the details of the electronic structure, it is important to obtain independent information on the electronic structure of the material. We also present the results of photoemission measurements performed on VPd$_3$ and compare the results with the electronic structure calculations.

The results of our calculations are easily summarized. While the paramagnetic calculation in the Cu$_3$Au structure yields a high density of states at the Fermi level, the TiAl$_3$ calculation yields a substantially smaller value. The spin-polarized configuration yields a magnetic moment of 1.23μ_B in the Cu$_3$Au structure, and the much smaller moment of 0.25μ_B in the TiAl$_3$ structure. In part the reduction of the magnetic moment is due to a significant broadening of the density of states associated with vanadium d states. These results are in qualitative agreement with the recent calculations of Kübler based on the augmented-spherical-wave (ASW) method.[6] When the density of states is suitably broadened and compared with the photoemission data, we find that the results for the real, tetragonal structure agree quite well with experiment while the results for the hypothetical, cubic structure are in much poorer agreement.

CALCULATIONAL DETAILS AND RESULTS

The band-structure calculations presented in this paper were performed using the linear combination of muffin-tin orbitals (LMTO) method[7] including the combined correction terms to the atomic-sphere approximation. The programs used are basically those described in Ref. 8, but they were suitably modified by us for computing the electronic structure of compounds. A semirelativistic form of the wave equation was used,[9] similar to that of Koelling and Harmon,[10] in which spin-orbit interactions are neglected, but other relativistic corrections to Schrödinger's equation are included exactly. The Hedin—von Barth[11] form of the local-spin-density approximation to the exchange correlation potential was employed in all the calculations using the parameters of Janak.[12]

The calculations were carried out for a number of lattice constants near the experimentally determined values[13] of $a_0 = 7.272$ a.u. and $c_0 = 14656$ a.u. The c/a ratio of 2.015 is very close to the ideal value of 2.0. The volume per formula unit is 387.54 (a.u.)^3 at the equilibrium lattice constants.

Within spheres around each atomic center the wave function is expanded in muffin-tin orbitals. In our calculations muffin-tin orbitals through $l = 2$ were used in both the palladium and vanadium spheres for both cubic and tetragonal structures. The ratio of the radii of vanadium and palladium Wigner-Seitz spheres was chosen to be 1.

The calculation of the cubic VPd$_3$ electronic structure was performed on a mesh of 84 and 120 points in the irreducible $\frac{1}{48}$ of the Brillouin zone (BZ). Because the electronic structure converges rapidly when the LMTO method is used, the calculation may be repeated entirely for each sampling of the Brillouin zone. When the saturation magnetic moment differed by only a few percent between the two calculations, further sampling was deemed unnecessary. The calculation of the electronic structure on the TiAl$_3$ lattice was performed for 75 and 405 points in the irreducible $\frac{1}{16}$ of the centered tetragonal Brillouin zone. The saturation magnetic moment and $N(E_F)$ differed by only a few percent when the results from the two mesh samples were compared.

The mesh of Brillouin-zone points determines the vertices of tetrahedra for the evaluation of the density of states by the method of Jepsen and Andersen.[14] Each general point in the Brillouin zone defines six tetrahedra; points in symmetry planes define fewer tetrahedra. In the irreducible wedge of the cubic BZ 84 points generate 216 tetrahedra while 165 points generate 512 tetrahedra. In the irreducible wedge of the tetragonal BZ 75 points generate 192 tetrahedra while 405 points generate 1536 tetrahedra. The density of states was evaluated for increments of energy of 0.04 eV (0.003 Ry).

In order to demonstrate that the absence of magnetism is a structural effect, we first performed the calculation on the compound in the Cu$_3$Au structure. The DOS from the paramagnetic calculation is shown in Fig. 2. An angular momentum decomposition of the density of states shows that the states in the region from -6.0 to -0.4 eV below the Fermi level are composed primarily of palladium d character. The remarkable feature of the DOS is the very sharp, narrow peak which is due to vanadium d states. The density of states at the Fermi energy [$N(E_F)$] is very large, over 10 states/eV unit cell; however, since the peak is so sharp, the value of $N(E_F)$ may not be reliable. The DOS resulting from the spin-polarized calculation of the Cu$_3$Au structure is shown in Fig. 3. The magnetic moment which develops has a magnitude of 1.23μ_B in reasonable agreement with the 1.4μ_B reported by Wil-
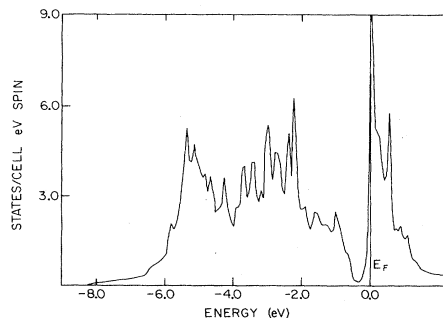

FIG. 2. The total density of states for paramagnetic VPd$_3$ in the Cu$_3$Au crystal structure. The energy zero is at the Fermi level.
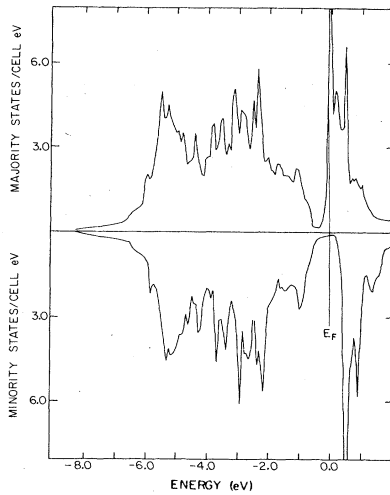
FIG. 3. The total density of states for spin-polarized VPd₃ in Cu₃Au structure.

FIG. 5. The total density of states for paramagnetic VPd₃ in the TiAl₃ crystal structure.

liams et al.[1] For the spin-polarized calculation, the magnetic moment and hydrostatic pressure[15] were evaluated as a function of lattice constant. The results are shown in Fig. 4. The theoretically determined equilibrium lattice constant in the cubic structure is within 1.4% of the value consistent with experimental volume per formula unit. The magnetic moment changes by less than ±1% of the value at equilibrium as the unit-cell volume is changed by ±15%.

The results for the compound in the TiAl₃ crystal structure differ markedly from those obtained for the hypothetical Cu₃Au structure. The density of states in the paramagnetic configuration is shown in Fig. 5. The major difference in the density of states is the broadening in the feature associated with vanadium d states. The DOS at the Fermi energy, 2.95 states/eV unit cell, is considerably
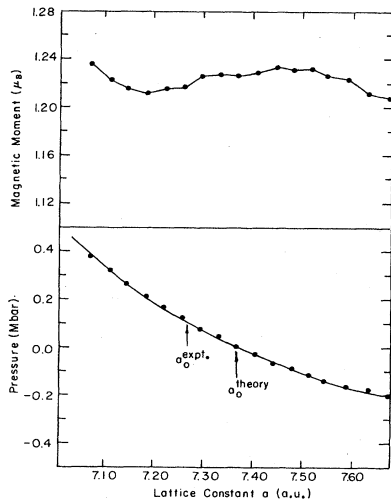
smaller than the value obtained in the cubic structure. The spin-polarized density of states is shown in Fig. 6. The self-consistent spin-polarized electronic structure at the equilibrium lattice constant was actually calculated for three different initial guesses of the magnetic moment: $0.5\mu_B$, $0.05\mu_B$, and $0.01\mu_B$. For each initial value of the magnetic moment, the self-consistent value of the magnetic moment converged to $0.25\mu_B$. As shown in Fig. 7, the magnetic moment increases as the unit-cell volume is increased, but decreases slowly as the unit-cell volume is decreased. With a 15% reduction in unit-cell volume the magnetic moment is still $0.22\mu_B$. The result indicates no tendency for the magnetic moment to go to 0, the experimentally observed value.

The results of the present calculation may be compared with previously obtained experimental results. The smaller magnetic moment found for the tetragonal structure is in better agreement with the experimentally determined absence of vanadium local moments and magnetic ordering in VPd₃, but why a small moment persists at self-consistency remains a problem. Low-temperature specific-heat measurements have also been performed on VPd₃ (Ref. 16) and the values of the linear coefficient of

FIG. 4. Pressure (lower panel) and magnetic moment (upper panel) as a function of cubic lattice constant for spin-polarized VPd₃ in the Cu₃Au crystal structure.
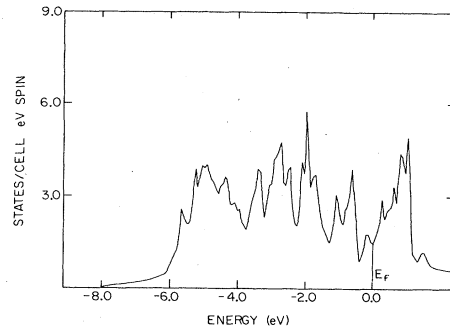

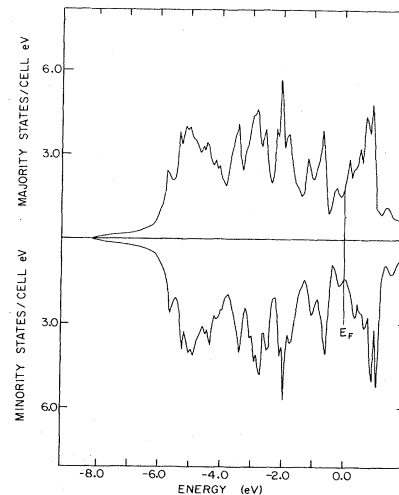FIG. 6. The total density of states for spin-polarized VPd₃ in the tetragonal structure.
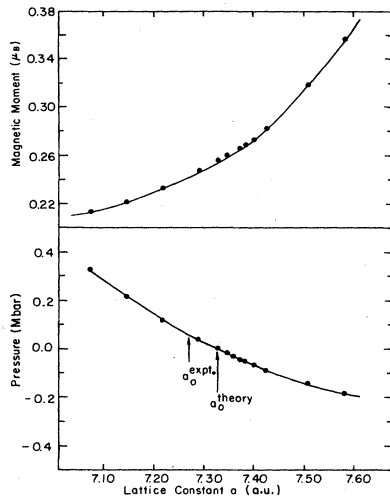
FIG. 7. Pressure (lower panel) and magnetic moment (upper panel) as a function of lattice constant a for spin-polarized VPd_3 in $TiAl_3$ crystal structure.
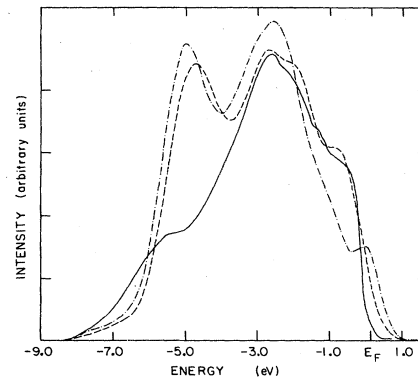

FIG. 8. The comparison of the density of occupied states with photoemission experiment. The solid line is the experimental energy distribution curve obtained with $h\nu = 21.2$ eV photons. A secondary electron contribution has been subtracted in an approximate way by extropolating the secondary electron peak to the Fermi energy. The dashed line ($-\ -\ -$) is the tetragonal DOS, and the cubic DOS is shown by a dashed-dotted line ($-\cdot-\cdot-\cdot$).

specific heat γ range from 3.7 $mJ/mol\,K^2$ for the ordered compound to 4.7 $mJ/mol\,K^2$ for the disordered system. Assuming the electron-phonon mass enhancement factor λ, which is not known for this system, to be zero, the DOS at the Fermi level derived from the heat-capacity data is 1.55 states/eV unit cell for the ordered compound and 1.99 states/eV unit cell for the disordered compound. Our calculated value of 2.95 states/eV unit cell is too large by 50%, but is in far better agreement than the result for the Cu_3Au calculation. Kübler obtains an even larger value for $N(E_F)$ in the $TiAl_3$ calculation of 3.6 states/eV unit cell. The best agreement by far between the theoretical value of $N(E_F)$ and γ has been obtained with the use of a non-self-consistent LCAO technique, which results in a value of $N(E_F)$ of 2.58 states/cell eV.[17] One difference between the LCAO calculation and both the present calculation and that of Ref. 6 is the inclusion of nonspherical components in the potential. The anisotropy in the potential may be an important contribution in broadening the vanadium d states which leads to a small value of $N(E_F)$. Although a smaller value of $N(E_F)$ does not necessarily lead to a smaller value of the magnetic moment, the two are often correlated. The fact that the calculated density of states is higher than the value inferred from specific-heat measurements suggest a reason for the nonvanishing magnetic moment found in the calculation.

EXPERIMENTAL DETAILS AND RESULTS

A polycrystalline sample of VPd_3 in the ordered $TiAl_3$ structure was prepared by arc melting and annealing techniques described previously.[2] The angularly averaged photoemission measurements were made in a Vacuum Generators ADES 400 system using the 21.2-eV line of a helium resonance lamp. The analyzer was operated at a pass energy of 20 eV and with a resolution of about 0.2 eV. The sample surface was cleaned in situ by repeated Ar-ion bombardment followed by an anneal. Auger electron spectroscopy revealed only traces of oxygen following the above procedure. With a base pressure of 5×10^{-11} Torr the sample remained clean for several hours.

The experimental results are compared with the calculation in Fig. 8. The calculated densities of states have been broadened with a Gaussian of width 0.35 eV to reflect the experimental broadening. It is clear from the figure that the DOS from the $TiAl_3$ structure is in much better agreement with the experimental results than that from the Cu_3Au structure for binding energies less than 5 eV. The features at -0.75, -2.0, and -2.8 eV are well reproduced in the DOS of the tetragonal structure. The feature in the theoretical DOS at -5.5 eV contains significantly more s character than the features at smaller binding energy. The cross sections between the s-like initial states and the photoemission final states are presumably small, which could explain the difference between the photoemission intensity and the calculated DOS near -5.5 eV.

DISCUSSION AND CONCLUSIONS

In this paper we have demonstrated that the crystal structure of a compound can have surprisingly great effects on the electronic structure of a material and, hence, on its physical properties. In the hypothetical Cu_3Au structure, VPd_3 is magnetic with a saturation moment of $1.23\mu_B$, but the magnetic state is not observed experimentally. When the proper crystal structure is taken into account, spin-polarized calculations yield a much smaller moment of $0.25\mu_B$. These results are qualitatively in agreement with a recent ASW calculation by Kübler. In addition we have shown that the theoretical result for the DOS in the actual tetragonal structure agrees quite well with photoemission results while the cubic structure results do not.

The result that a small but measurable magnetic moment is found in the centered tetragonal calculation remains a puzzle. The most likely explanation of the discrepancy lies in our use of a spherically averaged potential. The lower value of $N(E_F)$ in the tetragonal structure is a result of the reduced symmetry of the crystal structure. Including nonspherical components of the potential within the muffin-tin sphere might broaden the vanadium d state to further reduce the magnetic moment.

It is interesting to consider the case of VPt_3 as well. This compound can be synthesized in either the Cu_3Au or $TiAl_3$ structures. In both forms it is reported to be magnetic at low temperatures, but with the same small saturation moment of $0.1\mu_B$.[18] The results of electronic structure calculations on this compound in both structures yield results similar to those for VPd_3.[6] The difference between theory and experiment indicates that additional improvements are required in linearized band-structure methods for weakly magnetic materials. Photoemission results could prove very valuable in resolving the difference between theory and experiment for this compound as well.

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