Electronic Structure of Nearly Ferromagnetic compound HfZn$_2$

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The electronic structure of HfZn$_2$ has been studied based on the density functional theory within the local-density approximation. The calculation indicates that HfZn$_2$ shows ferromagnetic instability. Large enhancement of the static susceptibility over its non-interacting value is found due to a peak in the density of states at the Fermi level.

PACS numbers: 71.28.+d, 75.10.Lp, 71.18.+y, 71.20.Lp

I. INTRODUCTION

The discovery of ferromagnetic superconducting phase of ZrZn$_2$ has been revived both theoretical and experimental attention. Investigation the 5d compound HfZn$_2$ which has the same crystal structure (C15 cubic Laves structure) with the ZrZn$_2$ should be quite interesting. The lattice constant of HfZn$_2$(a=7.32Å) is very similar to that of ZrZn$_2$(a=7.39 Å). The isoelectronic isostructural material ZrZn$_2$ is nowadays considered a classic example of a Stoner-Wohlfarth itinerant weak ferromagnet. The magnetic moments of ZrZn$_2$ have been reported as very small magnetic moments(values from 0.12 to 0.23 µ$_B$). These do not saturate even at magnetic fields as high as 35T. The Curie temperature $T_C$ drops approximately linearly with pressure, starting at 29K at P = 0 and decreasing to 4K at P = 16 kbar, which extrapolates to a quantum critical point(QCP) at P = 18 − 20 kbar. We contend that the weak ferromagnetism of ZrZn$_2$ is an accidental consequence of its band structure: apparently $E_F$ is located near a sharp maximum in the density of states. If this picture is correct, then it should follow that the analogous 5d compound HfZn$_2$ which has the same crystal structure, and same number of d-electrons, should behave similarly.

Experiments show that HfZn$_2$ is an exchange enhanced paramagnet. Though the material does not manage to reach the ferromagnetic state, its susceptibility $\chi(T=0)$ is uniquely high among 5d systems and strongly temperature dependent; in fact, it is about the same as the susceptibility of the nearly ferromagnetic 4d element Pd ($\chi = 6.8 \times 10^{-4}$emu/mol). The measured susceptibility follows a Curie-Weiss law in the temperature range of 2K-294K. Such temperature dependence is found in rare-earth and some 3d elements, but it is unusual for a 4d and 5d compound. No other compound exhibits a Curie-Weiss susceptibility at low temperature but only 4d compound ZrZn$_2$ shows the temperature dependence. The measured susceptibility data can be expressed as $\chi(T) = \chi_0 + \frac{C}{T-\theta}$, and Knapp et al obtained $\theta = -160K$ and $\chi_0 = 167 \times 10^{-9}$ emu/mole. The negative Curie-Weiss $\theta$ does not result from antiferromagnetic order by their experiment. Such negative $\theta$ has been observed in the Kondo systems, which are dilute alloys of 3d transition metals in nonmagnetic hosts. In such systems the negative $\theta$ are taken as an indication of strong interactions between the local 3d moments and the conduction electrons of the hosts. When the negative $\theta$ are observed in an alloy, the Kondo resistivity minimum is also found. If HfZn$_2$ is related with the local moments like the dilute system, we can expect that HfZn$_2$ has a Kondo type resistance. Experiments show that the resistivity data follows $\rho = \rho_0 + AT^3$ for the temperature range of $T \leq 40K$, but no resistivity minimum occurred. They also measured the linear specific heat coefficient for HfZn$_2$ of $\gamma=15.8$ mJ/K$^2$ mole(formular unit). The large zero temperature magnetic susceptibility is much larger than that expected from the measured electronic specific heat coefficient $\gamma$, which indicates that exchange enhancement effects are sufficient enough to make the system ferromagnetic.

In this work, the precise self-consistent full potential local orbital minimum basis band structure scheme (FPLO) are employed to investigate the electronic and magnetic properties of HfZn$_2$ based on the density functional theory. We compare the electronic structures and magnetic properties between HfZn$_2$ and ZrZn$_2$. We focus on studying the effect of magnetism on the band structure, Fermi surfaces and compare them with the experimental results.

II. CRYSTAL STRUCTURE

HfZn$_2$ has same crystal structure with ZrZn$_2$. They crystallize into a C15 cubic Laves lattice. The C15 (AB$_2$) structure is a closely packed structure and the site symmetry is high for the two constituents. In this structure, Hf atoms occupy the positions of a diamond lattice while the Zn atoms form a network of interconnected tetrahedra. Since the major contributions to $N(E_F)$ come from Hf, the local environment of Hf atoms is particular important for our concerns. Each Hf is surrounded by Zn neighbours at a distance of 2.70 A and Hf neighbours 2.82 A away. HfZn$_2$ structure belongs to the Fd3m space group with Hf occupying the 8a site, and Zn the 16d site. The site symmetry of Hf is 43m and Zn has 3m site symmetry. We used experimental lattice constant (7.32Å) for our calculations. There are 2 formular units per cell.
III. METHOD OF CALCULATIONS

We have applied the full-potential nonorthogonal local-orbital minimum-basis (FPLO) scheme within the local density approximation (LDA).\cite{6} In these scalar relativistic calculations we used the exchange and correlation potential of Perdew and Wang.\cite{7} Hf 4s, 4p, 4d, 4f, 5s, 5p states and Zn 4s, 4p were included as valence states. All lower states were treated as core states. The inclusion of the relatively extended semicore states of Hf 4s, 4p, 4d, 5s, 5p and Zn 4s, 4p as band states was done because of the considerable overlap of these states on nearest neighbors. This overlap would be otherwise neglected in our FPLO scheme. The spatial extension of the basis orbitals, controlled by a confining potential \((r/r_0)^4\), was optimized to minimize the total energy. The self-consistent potentials were carried out on a \(k\) mesh of 24 \(k\) points in each direction of the Brillouin zone, which corresponds to 413 \(k\) points in the irreducible zone. A careful sampling of the Brillouin zone is necessitated by the fine structures in the density of states near Fermi level \(E_F\).

IV. RESULTS

We first show the full LDA non-magnetic band structure of HfZn\(_2\) in the Fig. \ref{fig:1}.\ref{fig:1} The very flat Hf 4\(f\) states lie at -11.5 eV. Another flat Zn 3\(d\) bands are located between -8.0 eV and -6.0 eV. Above them there are Zn 4\(s\) and Hf 6\(s\) bands. Those bands near Fermi level are mainly Hf-centered 5\(d\) states with hybridization of Zn 4\(s\). The Zn 4\(s\) states cross the Fermi level at the symmetry point \(\Gamma\) with hybridization of Hf \(dxy\), \(dyz\) and \(dz\) states, which make the ball-like Fermi surface (FS). Here we compare the band structures between HfZn\(_2\) and ZrZn\(_2\) with more details in the Fig. \ref{fig:2}. While the Zr 4\(d\) states are important near the Fermi level, Zr 4\(d\) states are important near the Fermi level.

FIG. 1: The full LDA bandstructures of non-magnetic HfZn\(_2\) along symmetry lines, showing that there are several bands with dispersion being of primarily Hf 5\(d\) and Zn 4\(p\) characters near the Fermi level.

FIG. 2: Top panel: The LDA non-magnetic band structure of HfZn\(_2\) showing that the Hf 5\(d\) states play dominant roles near the Fermi level. Bottom panel: Band structure of ZrZn\(_2\); the Zr 4\(d\) states are important near the Fermi level.
V. DISCUSSION

Motivated by the observation of Curie-Weiss susceptibility in weakly ferromagnetic metals such as ZrZr$_2$ and Sc$_3$In where the local moment picture is clearly inadequate, Moriya et al. [9, 10] developed a theory called self-consistent renormalization (SCR) theory of ferromagnetic metals. A self-consistent treatment needs to calculate dynamical susceptibility $\chi(q, \omega)$ and free energy so that the static long wavelength limit of the dynamical susceptibility agrees with that calculated from the renormalized free energy. Ogawa [11] did an experiment with the Zr$_{1-x}$Hf$_x$Zr$_2$, which is consistent with the SCR features.

Moriya and Kawabata [8] discussed the importance of the effects of spin fluctuations on magnetic properties of weak itinerant ferromagnets. Spin fluctuations affect also an electrical conductivity of weak itinerant ferromagnets. It gives a large enhancement of the electrical resistivity at low temperature. Mills and Lederer [12] found out that $T^2$ dependence of resistivity is a general feature of a Fermi liquid in a low temperature range. Mathon [13] discussed the temperature dependence of resistivity of weak ferromagnets near their critical concentration, giving a result of $T^{5/3}$ dependence. Ueda and Moriya [14] developed a theory of electrical and thermal resistivities on the basis of Moriya and Kawabata’s studies, which treated the spin fluctuation effect in a self-consistent way and has given a good explanation of the magnetic properties observed in weakly and nearly ferromagnetic metals. They give expressions to the resistivity of weak ferromagnets not only in low and high temperature limits but also in intermediate temperature region including $T_c$. Their theory clearly shows that the spin fluctuation effect is demonstrated not only in the magnetic properties but also in the electrical conduction of weak itinerant ferromagnets. According to the experiment by Knapp et al. the resistivity data of HfZn$_2$ follows the formular $\rho = \rho_0 + AT^3$ for the temperature range of $T \leq 40$K where $A = 1.1 \times 10^{-4} \mu \Omega$ cm/deg and $\rho_0 = 36 \mu \Omega$ cm. The $T^3$ term is indicative of strong $s-d$ scatter, and this result does not follow the theory of Moriya et al. [9].

Even though we can learn the some physical properties of HfZn$_2$ from the results of Ogawa and Knapp’s experiments, further studies are required in both experiment and theory. For example the Curie-Weiss temperature dependence of $\chi$ of ZrZn$_2$ and HfZn2 shows the charac-
teristics of localized moments behaviors. But the large $T^3$ in the resistivity and magnetic behavior ZrZn$_2$ below $T_c$ are indicative of the itinerant model. Therefore the both model should be incorporated to explain this phenomena.

VI. CONCLUSIONS

In this article we presented the electronic band structures of HfZn$_2$ and compared them with the ZrZn$_2$. In the band structure of HfZn$_2$, Hf 5d states play dominant roles near the Fermi level while Zr 4d states are important in the ZrZn$_2$. The presence of the peak close the Fermi level in the Density of states of HfZn$_2$ suggests that a very small hole or electron doping can drive system into ferromagnetic regime. The experiments show that HfZn$_2$ is located at the boundary between non-magnetic and ferromagnetic ground state. Our fixed spin moment calculations show that HfZn$_2$ has the magnetic instability, which is in agreement with the experiment. Since HfZn$_2$ is near the boundary of a non-magnetic and ferromagnetic state, the experiment for the phase transition from paramagnet to ferromagnet would be very interesting. Also the experimental investigation of the resistance behavior in the broad range of temperatures should be quite interesting.

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