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Hydrogen-induced modifications to the electronic structure of intermetallic compounds

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Abstract

First principles electronic structure calculations are reported for hydrogen absorbing intermetallic compounds belonging to an important class of Laves phases: the superconducting AB_2 compounds (with A=Zr, Hf; B=V). The C-15 Laves phases $Zr_xHf_{1-x}V_2$ have a maximum superconducting critical temperature of $T_c^{max} = 10$ K for $x = 0.5$. The large value of the electron–phonon coupling constant of these intermetallic compounds is mainly associated with the existence of high peaks in the density of states (DOS) at the Fermi energy, E_F. In contrast, the hydrogen-rich phases are not superconducting. We analyze the modifications in the electronic states at E_F due to the formation of hydrides and discuss the observed changes in the superconducting properties, the magnetic susceptibility and the electronic specific heat coefficient. The metal–hydrogen interactions are analyzed in terms of partial wave decomposition of the DOS. These results are used to interpret the available photoemission and X-ray emission spectra.

Keywords: Superconductivity; Hydrides; Intermetallic compounds; Electronic structure

1. Introduction

Among the intermetallic compounds, the Laves phases have been widely investigated in connection with their superconducting and magnetic properties [1], and also as structural materials due to their high melting temperature and high strength, and as hydrogen storage materials. Besides the rich field of potential applications of the Laves phase hydrides, an understanding of the modifications of the electronic and magnetic properties on hydrogen absorption is of fundamental interest.

In the superconducting AB_2 Laves phases, with A = Zr, Hf and B = V, with superconducting critical temperatures $T_c = 8$ K for ZrV_2 and $T_c = 9$ K for HfV_2 [2], the electron–phonon coupling is expected to be strongly affected by both the lattice expansion and the change in the nature of the electronic states at E_F on hydrogen absorption.

Using ab-initio band structure calculations, we studied the electronic properties of superconducting ZrV_2 and HfV_2 and analyze their modifications in the corresponding hydrogen-rich phases.

2. Computational method

The band structure calculations were performed using the local density approximation (LDA) of the density functional theory (DFT). We used the self-consistent linear muffin-tin orbitals method (LMTO) within the atomic sphere approximation (ASA), and the so-called combined correction terms were included to account for the overlap of the atomic spheres. Scalar relativistic corrections were taken into account, but spin–orbit coupling was ignored. The exchange and correlation term of the crystal potential was calculated within the von Barth–Hedin approach. The sampling of the Brillouin zones was carefully tested and the densities of states were calculated in a 1-mRy mesh with the linear energy tetrahedron method.

3. Results and discussion

ZrV_2 crystallizes within the C-15 cubic phase above $T_m = 100$ K and undergoes a martensitic rhombohedral distortion below this temperature [3]. The interplay between structural and superconducting transitions, also observed in A-15 superconducting materials such as V_3Si and Nb_3Sn, was widely discussed in the mid-1970s since the two transitions are indicative of a large electron–phonon coupling.

In this paper we focus mainly on the electronic structures of the intermetallic compounds in their high temperature cubic phases and on their hydrides.

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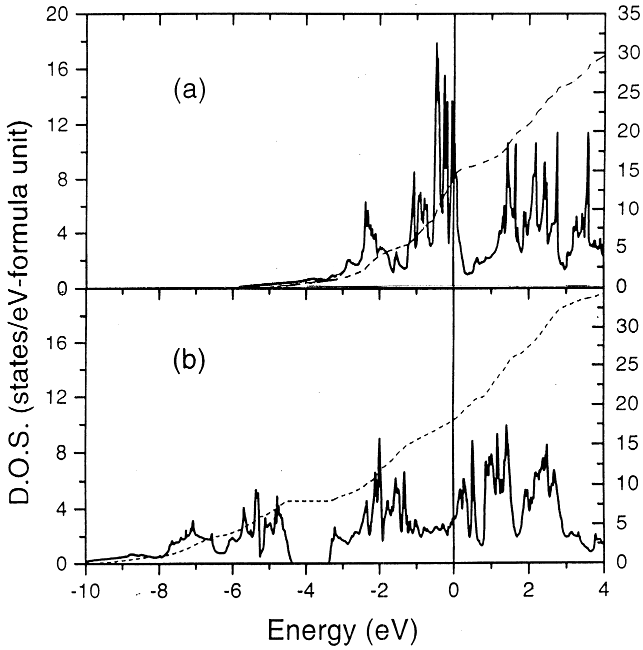

Fig. 1. Total densities of states, full line curves, left-hand-side scales; number of electrons, dashed line curves, right-hand-side scales. (a) ZrV_2 high temperature C-15 cubic phase, (b) ZrV_2H_4.

The total density of states of the cubic phase of ZrV_2 is plotted in Fig. 1a. The Fermi energy falls in the transition metal (TM)–d bonding bands close to a peak of the DOS. In agreement with previous work [4,5] the DOS at E_F is found to be high and dominated by the V 3d states, which give a much larger contribution at E_F than the Zr 4d states, as shown in Table 1. The large value of the DOS at E_F, 11.98 states of both spins/eV unit cell, is consistent with the large magnetic susceptibility [2], 3.8 emu/g-atom above T_m, as well as with the value of the electronic specific heat coefficient γ obtained from low temperature microcalorimetry [2,6]. In the rhombohedral phase, due to the symmetry lowering, the Van Hove singularities of the DOS are considerably smoothed. The total DOS at E_F is found to decrease by 35% from its value in the cubic phase. This result is consistent with the sharp decrease of the magnetic susceptibility observed at T_m [2]. It is interesting to point out in this connection that two distinct superconducting transitions differing by 1 K have been observed experimentally [7]. It was suggested that the two phases are superconducting, with the higher T_c value attributed to small amounts of untransformed cubic C-15 phase.

Table 1
Total density of states at the Fermi energy $N(E_F)$ and the partial densities of states of s, p, d, f types of atomic sites (states/eV unit cell both spin) of the intermetallic compounds in their high temperature cubic phases, and their hydrides

	$N(E_F)$	Atom	n_s	n_p	n_d	n_f
ZrV_2	11.98	Zr	0.03	1.16	1.53	0.09
		V	0.06	0.75	3.18	0.09
HfV_2	7.53	Hf	0.02	0.65	1.15	
		V	0.04	0.56	2.25	
ZrV_2H_4	3.26	Zr	0.01	0.05	0.60	
		V	0.01	0.08	1.14	
		H	0.01	0.03		
HfV_2H_4	2.81	Hf	0.01	0.02	0.41	
		V	0.01	0.08	1.02	
		H	0.01	0.03		

The electronic structure of ZrV_2H_4 was calculated using the structural data of Didisheim et al. [8] in the low temperature tetragonal phase in which the H atoms order at one of the Zr_2V_2 sites. The corresponding total DOS is plotted in Fig. 1b. The metal–H bonding states form four bands per formula unit, extending from −10.3 and −4.4 eV below E_F. In this energy range, the hydrogen interaction with Zr is slightly larger but of the same order of magnitude as that with the V states. The contribution of the transition metal (TM) d states to the metal–H bonding is dominant, followed by the TM p and to a lesser extent TM s contributions.

The DOS at E_F, which amounts to 3.26 states of both spins/eV unit cell, is much lower than in the pure intermetallic.

In the hydride, as in the pure intermetallic, the states at E_F mostly have a V d character. In contrast to the pure intermetallic, the TM p contribution at E_F is much smaller. The TM p states are found to participate in the metal–hydrogen low energy states.

The total densities of states of the high temperature cubic phase of HfV_2 is plotted in Fig. 2a. Besides small

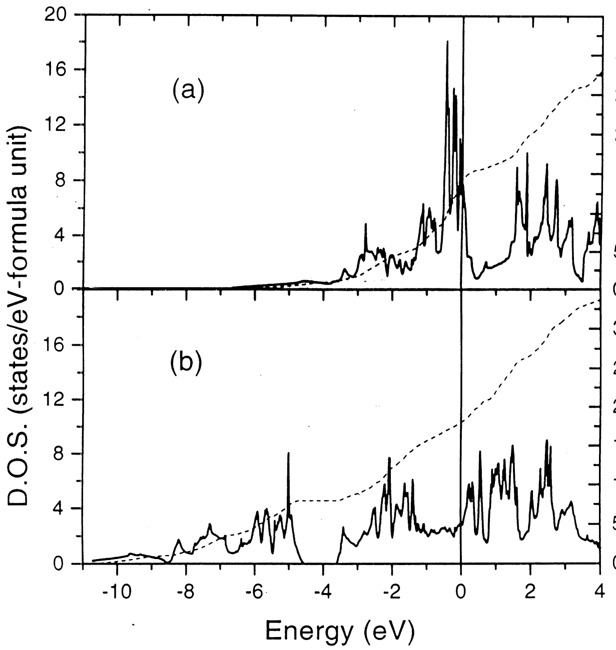

Fig. 2. Total densities of states, full line curves, left-hand-side scales; number of electrons, dashed line curves, right-hand-side scales. (a) HfV_2 high temperature C-15 cubic phase, (b) HfV_2H_4.

differences in the band widths due to different lattice parameters and spatial orbital extension, the general features are similar to those describes above for ZrV_2. As in ZrV_2, E_F is close to a peak of the DOS. The decrease in the value of the DOS at E_F associated with the lattice distortion in the low temperature phase amounts to $\approx 10\%$; it is found to be smaller than for ZrV_2. The DOS of HfV_2H_4 calculated with structural low temperature ordered phase data [9] is plotted in Fig. 2b. It is characterized by low energy TM–H bonding states of total width ≈ 6 eV. The Hf contribution to the metal–H bonding is larger but of the same order of magnitude as the V–H interaction. In the hydride, the DOS at E_F decreases by 62.7% from its value in the pure intermetallic.

The band width and structures obtained in the calculated DOS of ZrV_2 and ZrV_2H_4 are in good agreement with UV and X-ray photoemission data [10] and X-ray emission spectroscopic results [11].

Dreßler et al. [12] studied the effect of suppression of the martensitic phase transformation on the superconductivity; they found that quenching of the cubic phase resulted in a small decrease of the superconducting transition of the order of 1 K.

The results of electronic structure calculations can be used in conjunction with experimental data on the vibrational properties to estimate the electron–phonon coupling constant λ which essentially determines the value of the superconducting transition temperature T_C. In his study of transition metals, McMillan [13] showed that λ can be written in terms of the ratio of an 'electronic' contribution η to a 'phonon' contribution. For compounds with a large mass ratio between the two constituent atoms, such as metal hydrides, an approximation for λ has been proposed:

$$\lambda \approx \frac{\eta_{\mathrm{metal}}}{M_{\mathrm{metal}}\langle\omega^2\rangle_{\mathrm{acoustic}}} + \frac{\eta_{\mathrm{H}}}{M_{\mathrm{H}}\langle\omega^2\rangle_{\mathrm{optic}}} = \lambda_{\mathrm{metal}} + \lambda_{\mathrm{H}} \tag{1}$$

where M is the atomic mass, $\langle\omega^2\rangle$ is the second moment of the renormalized phonon frequencies, and the electronic contribution η is the product of the DOS at E_F by the mean square of the electron–phonon matrix element $\langle I^2\rangle$, as defined by McMillan [13]. Using the rigid-ion approximation and expanding the Bloch functions into their angular momentum representation, Gaspari and Gyorffy [14] showed that the electronic contribution at the K site, η_K, can be conveniently expressed in terms of quantities obtained from ab-initio band structure calculation; they have shown that

$$\eta_{\mathrm{K}} \approx \frac{E_{\mathrm{F}}}{N_{\uparrow}(E_{\mathrm{F}})\Pi^2}\sum_l 2(l+1)\sin^2(\delta_{l+1}^{\mathrm{K}} - \delta_l^{\mathrm{K}}) \times \frac{n_l^{\mathrm{K}}(E_{\mathrm{F}})\,n_{l+1}^{\mathrm{K}}(E_{\mathrm{F}})}{n_l^{\mathrm{K}(1)}(E_{\mathrm{F}})\,n_{l+1}^{\mathrm{K}(1)}(E_{\mathrm{F}})} \tag{2}$$

where δ_l^K is the single site scatterer phase shift at the Fermi energy E_F, n_l^K the partial density of states (DOS) of angular character l at the K site, $n_l^{K(1)}$ is the corresponding partial DOS of a free scatterer and $N_{\uparrow}(E_F)$ the total DOS per spin, at E_F.

At the metal sites, the electronic contribution η_{metal} is found to be dominated by the p–d scattering mechanism. The d–f term is much smaller, particularly at the Zr site. For ZrV_2, in its cubic C-15 phase, η_{metal} amounts to 5.8 eV/(Å)^2.

At the H sites, the s phase shifts are close to the value $\pi/2$. However, in this hydride, the partial DOS of s type at the H site at E_F is extremely small because E_F falls in the TM d bands unlike in superconducting Pd–H where metal d bands are filled. η_H is estimated to only 0.1 eV/(Å)^2. Thus the total value of the electronic term η decreases by 78% from the pure intermetallic to the hydride due to a drastic reduction of the contribution at the metal sites and to the negligible value of η_H. The absence of detailed experimental data on the phonon contributions precludes further estimation of λ.

Nevertheless, it is clear that the observed disappearance of superconductivity in the hydrogen-rich compound is associated with the drastic decrease in the total DOS at E_F as well as with the change in the character of the electronic states of p type at E_F.

4. Conclusions

We have studied the hydrogen-induced modifications to the electronic structure of the superconducting Laves phases ZrV_2 and HfV_2. We show that the electronic contribution of the electron–acoustic phonon coupling is drastically reduced due to a large decrease of the DOS at E_F on hydrogen absorption and a change in the orbital character of the states. The electronic contribution of the electron–optical phonon is very small because the Fermi level of the hydride falls in the TM d bands. For these reasons, the hydrides are not superconducting.

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