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Experimental and theoretical study of the electronic structure of Fe₃Al

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Abstract

The electronic structure of Fe₃Al is studied by X-ray absorption near-edge spectrum (XANES) at the Fe K edge. The XANES spectrum is compared with that calculated by theory. The experimental XANES features for this intermetallic compound reflect the Fe-p unoccupied density of states (DOS). The magnetic moments and the DOS at the Fermi energy at different atomic sites and spins are calculated and compared with experimental and other theoretical values. The number of Fe d electrons in Fe₃Al is calculated to be 6.25.

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1. Introduction

Fe₃Al has a number of unusual electronic and magnetic properties that make it attractive for high-temperature applications. It is a ferromagnetic metal with $T_c = 713$ K and magnetic moment of $2.2 \mu_B$ and $1.45 \mu_B$ for two different Fe sites [1]. Its magnetic property is coupled strongly to its crystalline structure. Fe₃Al has the DO₃ structure with a lattice constant of $5.789 \text{ \AA}$ [2], which is shown in the third column in Table 1 along with the theoretical lattice constants obtained in the present calculation. In this paper, X-ray absorp-

tion near-edge spectrum (XANES) at the Fe K edge of Fe₃Al was measured and was compared with theoretical XANES spectrum. Such analysis is especially important for establishing a relationship between the experimental XANES spectrum and the unoccupied part of the local density of states (DOS) and obtaining quantitative information about hole numbers and charge transfer in this intermetallic compound. The total and site- and spin-decomposed magnetic moments and DOS's at the Fermi energy ($n(E_F)$) of Fe₃Al are calculated and compared with corresponding experimental and theoretical values. This paper is organized as follows. In Section 2 the experimental and the theoretical methods are described. In Section 3 the results and discussion are presented. The conclusions of this work are contained in Section 4.

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Table 1

Crystal structure, lattice constant a , total DOS at the Fermi energy $n(E_F)$ and bulk modulus for Fe_3Al

Material	Crystal structure	a (Å)	$n(E_F)$ (states/eV cell)	B (Mbar)
Fe_3Al	DO_3	5.645	11.73	2.042
		5.761	2.78	1.666
		5.789	3.09	

The first, second and third line shows the theoretical (paramagnetic), theoretical (ferromagnetic) and experimental values, respectively.

2. Methods

2.1. Experimental methods

The Fe_3Al polycrystalline sample was prepared by arc melting the weighted amounts of 99.9 at.% pure Fe and 99.999 at.% pure Al (molar mass ratio of Fe:Al = 3:1) together under an argon atmosphere. It was then annealed in an evacuated ($\sim 10^{-6}$ Torr) quartz tube at 1200 °C for 96 h to improve the homogeneity, and quenched into a water bath. The total loss of weight during these processes was 1.53%. The button was then cut and polished to obtain mirror-like surface. Powder X-ray diffractometry showed that the Fe_3Al sample is a single phase of the DO_3 structure. Energy dispersive X-ray (EDX) analysis showed that the molar ratio of Fe:Al is 2.22:1 (i.e. $\text{Fe}_{0.69}\text{Al}_{0.31}$). The residual resistivity (ρ) ratio ($\text{RRR} = (\rho_{300\text{ K}} / \rho_{4.2\text{ K}})$) for Fe_3Al (2.3) is about 20% less than that (2.9) reported previously [3]. The XANES experiments were carried out on wiggler beamline 17 C at the Synchrotron Radiation Research Center, Taiwan. A Si(111) double-crystal monochromator was used and the typical energy resolution was about 2 eV. The XANES spectra were collected by recording the total yield of secondary electrons from the sample surfaces at room temperature. Standard 5- μm -thick Fe foil was used as reference for energy calibration. Its XANES data were also used as reference spectrum. The photon flux was obtained simultaneously by measuring the current of a Au mesh located near the exit slit of the monochromator and used for normalization of the XANES spectra.

2.2. Theoretical methods

In order to calculate the theoretical XANES spectrum and other physical parameters of Fe_3Al , we use the highly accurate all-electron full-potential linear augmented-plane-wave (FLAPW) method [4]. The calculations are based on the first-principles density functional theory with the generalized gradient approximation to the exchange-correlation potential [5]. We begin the calculations by determining total energies at several values of the lattice constants near the experimental one for Fe_3Al . These energies are then fitted to the Murnaghan equation of state to obtain the theoretical equilibrium lattice constants and bulk moduli. The muffin-tin radius of 1.24 Å is used for all the atoms. The wave functions, the charge densities, and the potentials are expanded in terms of the spherical harmonics inside the muffin-tin spheres. The cut-off angular momentum (l_{max}) is 10 for the wave functions and six for the charge densities and the potentials. The Brillouin zone (BZ) integration is carried out by using the improved tetrahedron method [6]. The number of the augmented plane waves included is about 90 per atom, i.e. $R_{\text{mt}}K_{\text{max}} = 9$ [4]. The number of the k points in the irreducible BZ wedge (IBZW) used in the self-consistent calculations is 47. To calculate the DOS curves and the theoretical XANES spectra, 165 k points in the IBZW were used. We have checked the convergence of the calculated eigenvalues with respect to the number of augmented plane waves used and the number of k -points used.

3. Results and discussions

The calculated total energy of the ferromagnetic Fe_3Al phase is lower than that of the paramagnetic one by 1.13 eV per formula unit. Thus, the XANES spectrum obtained from the spin-polarized calculation is used to compare with the experimental spectrum. The experimental (open circles) and theoretical (solid line) XANES spectra of Fe K edge for Fe_3Al are depicted in Fig. 1. Also shown in Fig. 1 is the Fe p partial DOS (dashed line) calculated for Fe_3Al . The maxima of the experimental XANES spectrum in Fig. 1, which

Fig. 1. The experimental (open circles) and theoretical (solid line) Fe K-edge XANES spectra for Fe_3Al . Also shown is the Fe p partial DOS (dashed line).

correspond to Fe 1s to ϵp transitions, coincide with the peaks in the Fe p partial-DOS curve. The zero energy corresponds to the inflection point of the Fe K-edge absorption edge (7112.5 eV). The experimental data were normalized to the theoretical spectrum in the region 10–20 eV above the absorption edge. Overall, we have a reasonable good agreement between theory and experiment. The white-line position and intensity and the absorption peaks at 0.5, 18.5 and 27.5 eV above the white-line energy are well reproduced in the theoretical spectrum. Small discrepancies in peak positions and peak intensities between theoretical and experimental spectra might be due to the use of the generalized gradient approximation in density functional theory and to the neglect of the core-hole effects. The decrease in peak height after the maximum in the theoretical XANES spectrum is due to the finite sized, linearized energy-dependent basis sets in the muffin-tin spheres used in the present calculation. For comparison, the corresponding graphs for Fe metal are shown in Fig. 2. One can see that the agreement between the theoretical and experimental spectra is better for Fe metal than for Fe_3Al , especially for energies larger than 25 eV above the white-line energy.

The calculated and experimental total $n(E_F)$ values for Fe_3Al are listed in the fourth column in Table 1, and the site- and spin-decomposed $n(E_F)$ values are listed in Table 2. The total $n(E_F)$ value

Fig. 2. Same as in Fig. 1, except for Fe metal.

Table 2

Magnetic moment M_s (the first line in units of μ_B/atom) and DOS at the Fermi energy $n(E_F)$ (the second and third lines for spin up and down states, respectively, in units of states/eV cell) at different atomic sites for Fe and Fe_3Al

Material	Fe(I)	Fe(II)	Al	Interstitial	Total
Fe	2.30			−0.06	2.24
	0.82			0.02	0.84
	0.23			0.03	0.26
Fe_3Al	2.44	1.96	−0.11	−0.21	6.04
	0.20	0.36	0.03	0.07	0.66
	0.07	1.83	0.06	0.16	2.12

for ferromagnetic Fe_3Al is 2.78 states/eV cell, which yields the electron–phonon mass enhancement factor of only 0.11 when compared with the experimental value (3.09 states/eV cell) [7] of DO_3 Fe_3Al obtained from specific-heat measurement. We note that the experimental $n(E_F)$ value for Fe_3Al could increase by a maximum of 20% from the above-sited value when the sample was heat-treated [7]. This is because various heat treatment of Fe_3Al changes the local atomic environment of the Fe atoms to form different phases [8]. The ferromagnetic $n(E_F)$ value for Fe_3Al in Table 1 is essentially the same as that (2.75 states/eV cell) [9] obtained from a previous self-consistent calculation and is much smaller than earlier non-self-consistently calculated value (5.79 states/eV cell) [10]. From Table 2, one can see that the $n(E_F)$ value of Fe(I) atoms in Fe_3Al is quite similar to that of Fe metal, but that of Fe(II) atoms in Fe_3Al

is considerably larger. This implies that the contribution to the total $n(E_F)$ value for Fe_3Al is dominated by the spin-down Fe(II) 3d electrons, which was confirmed by earlier electrical-resistivity study [3]. The calculated paramagnetic and ferromagnetic values of the bulk modulus (B) for Fe_3Al are 2.042 and 1.666 Mbar, respectively, and are listed in the last column in Table 1. The previously reported theoretical B values (1.59 ([8]) and 1.83 ([11]) Mbar) for Fe_3Al are close our ferromagnetic B value. To our knowledge, there is no experimental B value reported for Fe_3Al .

In Table 2, the calculated site-projected and total magnetic moments (M_s) are listed in the first row for Fe and Fe_3Al . For Fe_3Al , the M_s value is $2.44 \mu_B/\text{atom}$ for the Fe atoms on sites with eight Fe nearest neighbors (Fe(I) atoms), $1.96 \mu_B/\text{atom}$ for the other Fe atoms on sites with four Fe and four Al nearest neighbors (Fe(II) atoms), and $-0.11 \mu_B/\text{atom}$ for the Al atoms. These values are close to those reported previously by other theorists (2.4, 1.8, and $-0.13 \mu_B/\text{atom}$, respectively) [11] and experimentalists (2.2 and $1.45 \mu_B/\text{atom}$, respectively, for the Fe(I) and Fe(II) atoms) [1]. Earlier experimentalists [12], using neutron-diffraction measurement, reported similar M_s values for Fe_3Al at the Fe(I) ($2.18 \mu_B/\text{atom}$) and Fe(II) ($1.50 \mu_B/\text{atom}$) atomic sites. However, the M_s values (2.16 and $1.26 \mu_B/\text{atom}$, respectively) obtained from a non-self-consistent calculation [10] are smaller than those obtained from present self-consistent calculation. We should mention that, in Table 2, the Fe(I) atoms in Fe_3Al possess nearly the same M_s value as Fe atoms in bcc Fe metal, which also have eight Fe nearest neighbors. This observation was confirmed by neutron-diffraction study [13]. On the other hand, the difference between the M_s values of the Fe(II) atoms in Fe_3Al and of the Fe atoms in Fe metal is attributed to the increase of DOS near the top of the spin-down Fe 3d band in Fe_3Al . Thus, the Fe moment in Fe and Fe_3Al is only a function of the number of nearest Fe neighbors. The total M_s value for Fe_3Al is $6.04 \mu_B/\text{atom}$, which is close to the experimental values of $5.61 \mu_B/\text{atom}$ [14].

The number of d electrons calculated for Fe_3Al is 6.25, which is close to the value (6.59) reported previously [15]. The number of d electrons for Fe

metal calculated in this work is 6.15. The constancy in Fe d electrons between Fe metal and Fe_3Al is also observed in a lot of other metallic alloys [15].

4. Conclusions

The electronic structure of Fe_3Al is studied jointly by XANES measurement at the Fe K edge and by theoretical analysis using FLAPW method. A reasonable good agreement between theory and experiment is found. The experimental XANES features for this compound reflect the Fe-p unoccupied states.

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