

Magnetic and optical properties of Fe_2VAl and Fe_3Al

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Abstract

Full-potential linearized augmented plane wave plus local orbital method (FPLAPW + lo) calculations were performed for Fe_2VAl and Fe_3Al in order to investigate magnetic and optical properties and to show the origin of various optical transitions. It was found that the lattice constant and spin magnetic moments with the GGA method differ more from the respective experimental values than those calculated with the LSDA method. Furthermore, our calculated lattice constant and spin magnetic moments with the LSDA method were in overall better agreement with experiment. Our predictions agreed well with recent experimental reflectivity spectra. Meanwhile, the spectral peaks at the transitions were analyzed from the imaginary part of the dielectric function.

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1. Introduction

Recently, Heusler alloys have gained renewed interest due to their potential use as smart materials, for example, ferromagnetic shape memory alloys [1] or for developing spin-dependent electronics [2]. Fe_2VAl belong to a group of ternary Heusler-type compounds with the stoichiometric composition X_2YZ ordered in an L_{21} -type structure, many of which exhibit magnetic orders [3]. A Heusler alloy involves different transition metal atoms X and Y and a third element Z which is a non-magnetic metal or nonmetallic element. The Y and Z atoms occupy two fcc sublattices with the origins at $4a$ (0, 0, 0) and $4b$ ($1/2$, $1/2$, $1/2$), respectively. The X atoms are located at $8c$ ($1/4$, $1/4$, $1/4$) sublattices. Many experimental studies have been carried out on the magnetic properties in ferromagnetic Heusler alloys [3–8]. When V is replaced by Fe, the resultant structure is an intermetallic compound with a DO_3 crystal structure. The three Fe atoms per unit cell of Fe_3Al belonging to

two different types. The first type consisting of one Fe atom (denoted by Fe(I)) in the unit cell, is surrounded by eight Fe atoms in an octahedral coordination and the second type consisting of two Fe atoms (denoted by Fe(II)) in the unit cell, is surrounded by four Al and four Fe atoms in a tetrahedral coordination.

For recent years, there has been considerable interest in the electronic and optical properties of the two compounds Fe_2VAl and Fe_3Al . Okamura et al. measured near-normal incident reflectivity by using a Fourier interferometer [9]. The $\sigma(\omega)$ spectra were obtained from the measured $R(\omega)$ spectra using the Kramers–Kronig relations [10].

To better understand the physical properties of Fe_2VAl and Fe_3Al , we study the ab initio magnetic and optical properties of Fe_2VAl and Fe_3Al . We find that Fe_2VAl is a nonmagnetic compound unlike Fe_3Al , Heusler-type. Furthermore, the results of the present calculations explain some aspects of the previous electronic and magnetic measurements [11]. The organizations of the Letter follow as: we explain the computational method in Section 2. The electronic structure and optical properties are computed and discussed in Section 3. A brief conclusion is drawn in Section 4.

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2. Computational details

The present calculations were performed within the generalized gradient approximation (GGA) [12] and the standard local spin-density approximation (LSDA) to the density functional theory, as implemented in the Wien2k compute code [13], using the full potential linearized augmented plane wave (FPLAPW) method. In this method no shape approximation on either potential or the electronic charge density is made. We use Wien2k implementation of the method, which allows the inclusion of local orbitals in the basis, improving upon linearization and making possible a consistent treatment of semicore and valence states in one energy window, hence ensuring proper orthogonality. In the FPLAPW method, the unit cell is divided into two parts: (1) nonoverlapping atomic spheres (centred at the atomic sites) and (2) an interstitial region. The atomic sphere radii 1.8, 2.0 and 2.2 are used for Fe, V and Al, respectively, in the calculations. The convergence parameter RKmax ($R_{\text{mt}} \cdot K_{\text{max}}$, where K_{max} is the plane-wave cut-off and R_{mt} is the smallest of all atomic sphere radii), which controls the size of the basis sets in these calculations, is set to be 8.0. We have used $10 \times 10 \times 10$ meshes, which represent 1000 k -points in the first Brillouin zone for Fe₃Al and Fe₂VAl.

The imaginary part of the dielectric tensor is directly related to the electronic band structure of a solid, so it can be computed from the knowledge of the single-particle orbitals and energies approximated by the solutions of the Kohn–Sham equations. Assuming the one-electron, rigid band approximations, neglecting electron polarization effects (Koopmans' approximation) and in the limit of linear optics and of the visible–ultraviolet region [14,15], the imaginary part of the matrix element of the dielectric tensor is given by

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{i,f} \int_{\text{BZ}} \frac{2 dk}{(2\pi)^3} |\langle \varphi_{fk} | e \cdot p | \varphi_{ik} \rangle|^2 \times \delta(E_f(\omega) - E_i(\omega) - \hbar\omega). \quad (1)$$

For a vertical transition from a filled initial state $|\varphi_{ik}\rangle$ of energy $E_i(k)$ to an empty final state $|\varphi_{fk}\rangle$ of energy $E_f(k)$, with wave vector k , ω is the frequency, e the electron charge, m the free electron mass, and p the momentum operator.

With the help of the familiar Kramers–Kronig transformation, the real parts of the dielectric function can be related to its

imaginary parts $\varepsilon_2(\omega)$. Using $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, we calculated spectral reflectivity $R(\omega)$ [16] with a simple independent code.

3. Results and discussion

We first performed spin-polarized electronic structure by using the FPLAPW method for the Fe₃Al. The calculated LSDA, GGA, and experimental magnetic moments for the compound are reported in Table 1 and compared with available experiments. It is found that the lattice constant and spin magnetic moments with the GGA method differ more from the respective experimental values than those calculated with the LSDA method (see Table 1). Furthermore, our calculated lattice constants and spin magnetic moments with the LSDA method are in overall better agreement with experiment while other calculations give much higher values for spin magnetic moments and lower values for lattice constant. As a result, LSDA appears more accurate than GGA in calculating the electronic structures and optical properties of those compounds, so we will use it in all the calculations. The Fe(I) atom carries the largest moment (around $2.31174\mu_B$), while Fe(II) has a positive magnetic moment of about $1.83599\mu_B$. The total moment in the compound is $5.84114\mu_B$, which agrees well with experimental data. From above results it is found that the Fe(I) and Fe(II) atoms are the origins of magnetic properties of Fe₃Al. Our calculated magnetic moment appears to be slightly overrated with respect to experiment for Fe₃Al.

Figs. 1 and 2 show the LSDA spin-polarized band structures and total DOS and the partial DOS for the Fe₃Al in equilibrium. The lowest valence band (from -9.5 to -5.5 eV in both the majority and minority spin states) is almost entirely due to Al s electrons and is separated with respect to the other hybridized bands. As expected, the DOS around the Fermi level is heavily dominated by the 3d states of the Fe(I) and Fe(II) atoms, and the majority spin states are nearly fully occupied. The DOS curves for the minority spins exhibit a peak above the Fermi level due to Fe(I) and Fe(II) 3d effects. Particularly, at Γ of the band structures there is a series of twofold degenerate states (e_g) derived entirely from Fe(I) and Fe(II) d states and threefold degenerate states (t_{2g}) that allow hybridization of Fe(I) and Fe(II) d states with the Al p states. The spin band

Table 1

Theoretical lattice constant (a) and spin magnetic moments (m) in Fe₃Al. Experimental lattice constant and spin magnetic moments are also listed for comparison

Material	a (Å)	$m^{\text{Fe(I)}} (\mu_B)$	$m^{\text{Fe(II)}} (\mu_B)$	$m^{\text{Al}} (\mu_B)$	$m^{\text{interstitial}} (\mu_B)$	$m^{\text{Total}} (\mu_B)$
Fe ₃ Al (LSDA)	5.771	2.31174	1.83599	−0.0594	−0.09322	5.84114
Fe ₃ Al (GGA)	5.763	2.38553	1.93236	−0.0736	−0.21821	5.95824
Fe ₃ Al (exp)	5.793 ^f	2.2 ^a , 2.18 ^b	1.45 ^a , 1.50 ^b			5.61 ^c
Fe ₃ Al (cal)	5.761 ^a	2.51 ^d , 2.34 ^e	1.96 ^d , 1.89 ^e	−0.12 ^d	−0.21 ^d	6.10 ^d
	5.7626 ^e			−0.14 ^e		

^a Measured by T.J. Burch et al. (1979) [17].

^b Measured by S.J. Pickart and R. Nathans (1961) [18].

^c Measured by T. Wakiyama et al. (1972) [19].

^d Calculated by L.-S. Hsu et al. (2002) [20].

^e Calculated by G.Y. Guoy et al. (1998) [21].

^f Measured by W.B. Pearson et al. (1958) [22].

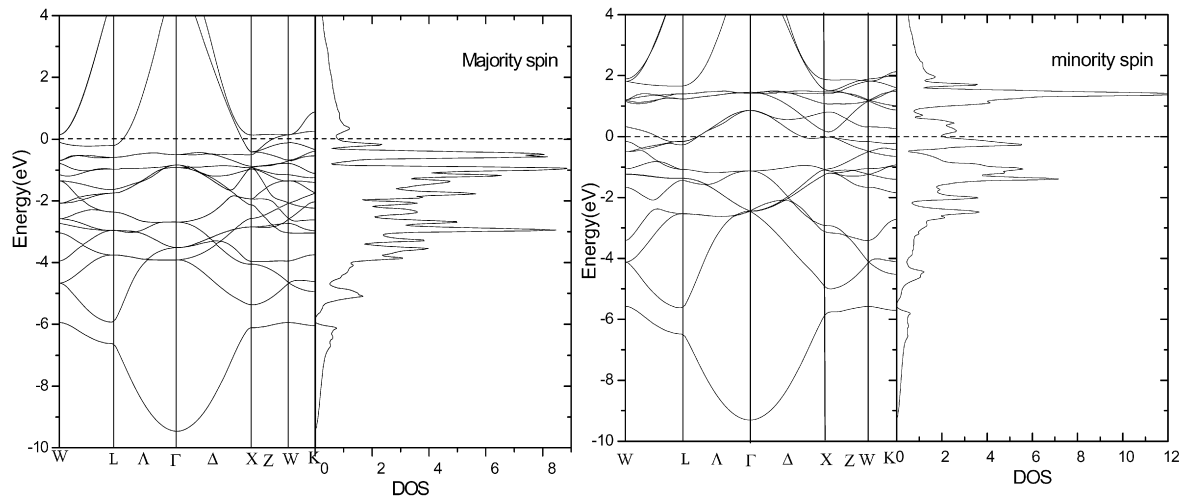


Fig. 1. Majority spin (left column) and minority spin (right column) band structures for Fe_3Al .

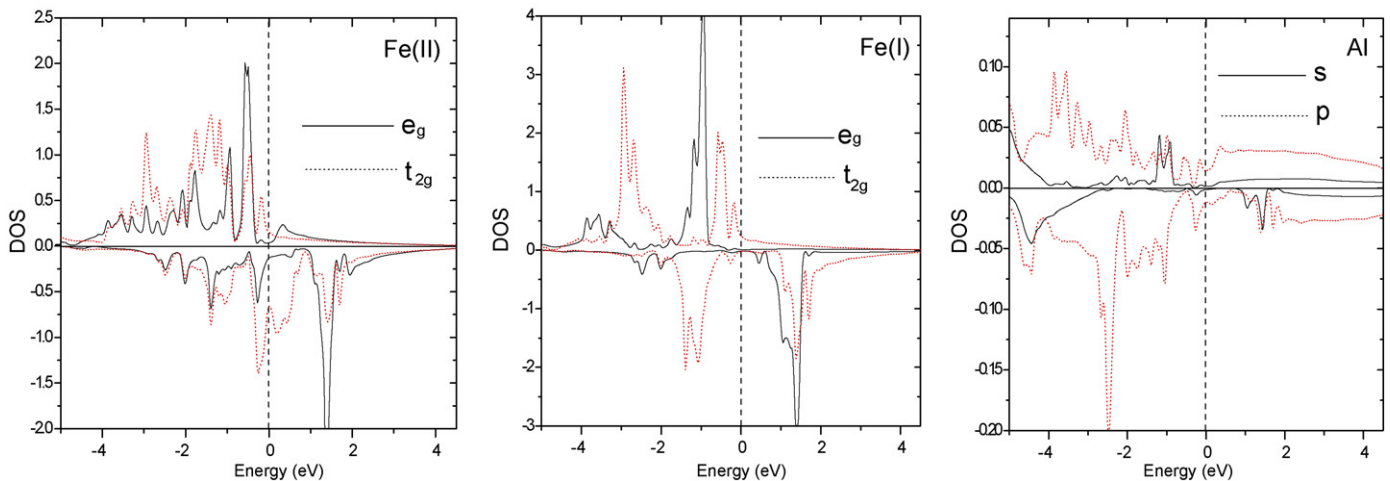


Fig. 2. Partial density of states of Fe_3Al .

structures of the majority and the minority indicate that Fe_3Al is metallic.

Further we show the LSDA band structure and the DOS for the Fe_2VAl in Fig. 3 at equilibrium. Since Fe_2VAl are non-magnetic [21], we did perform the spin-polarized calculations of Fe_2VAl , and, indeed, no difference from those of the non-spin-polarized calculations was found. Singh et al. [23] used the linear muffin tin orbital (LMTO) method to calculate the band structure and DOS with the LSDA; Weht et al. [24] used the linearized augmented plane wave (LAPW) method to calculate the band structure and DOS of Fe_2VAl with the LDA. Our calculated band structure is in good agreement with those of Singh et al. and Weht et al. It can be noticed that the calculated curves of DOS reveal similar structures to those of Singh et al. at the whole energy range. However, our results are quite different with those of Weht et al. Our highest peak of DOS arrives at 14 eV, whereas that of Weht et al. was around 7 eV.

As the reflectivity is one of the parameters which decide the optic figure of merit, it is of relevance to study the reflectivity as a function of energy. Fig. 4 shows the reflectivity spectra for the Fe_2VAl and Fe_3Al . As can be seen in the figure there is a close

match between our calculated results and the experiment [9] in the whole energy region for Fe_3Al . For the Fe_2VAl , our calculation is able to reproduce the overall trend of the experimental reflectivity spectra [9]. The good agreement between the theoretical and experimental optical spectra implies that the present calculations are able to well reproduce the other theoretical optical spectra of Fe_2VAl and Fe_3Al .

It has been earlier found that the calculated optical properties for LnSF ($\text{Ln} = \text{La}, \text{Ce}$) [25], CeBO_3 and CeB_3O_6 [26], SrX ($\text{X} = \text{Se}, \text{Te}$) [27], CaTiO_3 [28] and YBaMn_2O_5 [29] are in excellent agreement with the experimental findings, and we have therefore used the same theory to predict the optical properties of Fe_2VAl and Fe_3Al . To our knowledge, there are no experimental data concerning the imaginary part of the dielectric function for the Fe_2VAl and Fe_3Al . Fig. 5 shows our calculated imaginary part of dielectric function up to photon energy of 14 eV. The peak A and B D mainly comes from the electron transition from the Al 3p (VB) to Fe 3s (CB) orbitals. The peak C is mainly derived from the transition between Fe 3d (CB) and Al 3p (VB) orbitals. And the peak D is mainly derived from the transition among Fe 3d (CB), V 4s and Al 3p (VB)

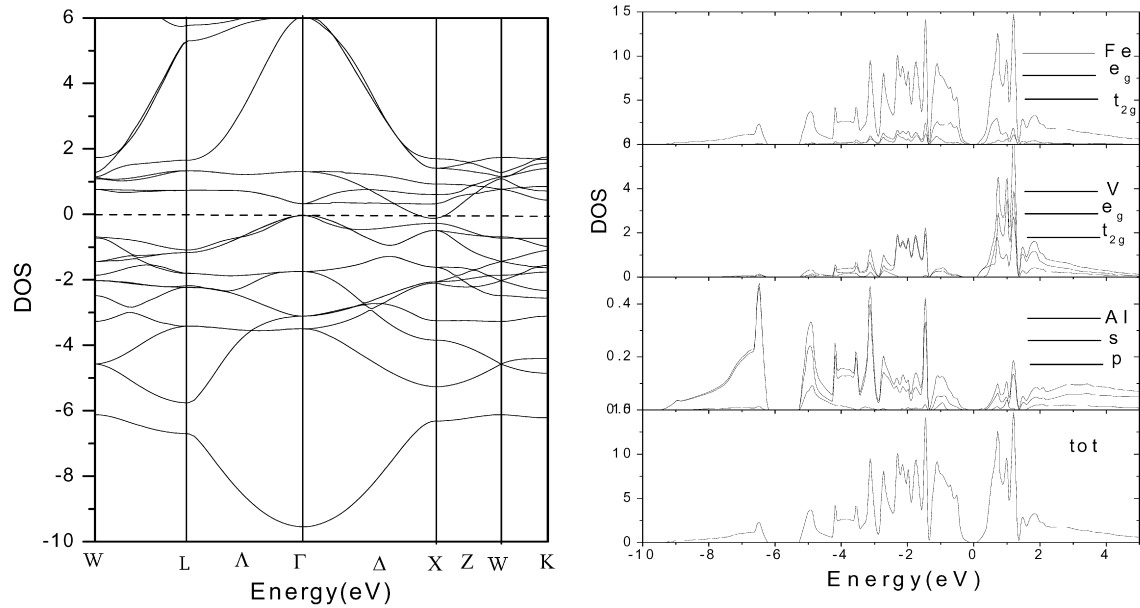
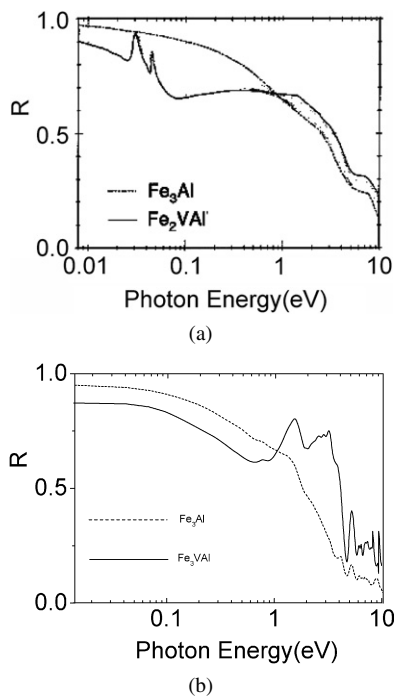
Fig. 3. Band structures and DOS for Fe_2VAI .

Fig. 4. Reflectivity spectra for Fe_3Al and Fe_2VAI . (a) Represents data taken from the experimental studies by H. Okamura et al. (Ref. [25]). (b) Represents the reflectivity spectra calculated from the $\varepsilon(\omega)$ spectra.

orbitals. Furthermore, the intra-band transitions also play an important role for these peaks. The optical properties of critical peaks are ascribed to the transitions of inner electron excitation from near VB semicore states to CB. The optical properties of critical peaks of E, F, G, H, I, J and K are ascribed to the transitions of inner electron excitation from near VB semicore states Fe 3d and Al 3s levels to CB. It is noted that a peak in $\varepsilon_2(\omega)$ does not correspond to a single interband transition since many direct or indirect transitions may be found in the band structure

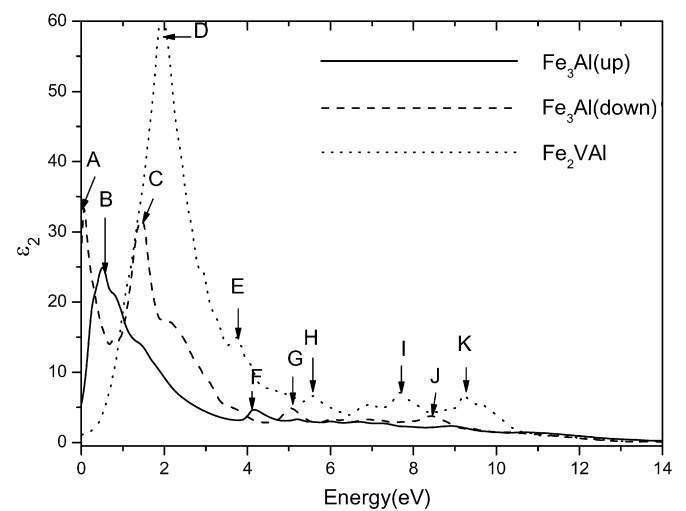


Fig. 5. Calculated imaginary parts of the dielectric function for Fe_3Al and Fe_2VAI .

with an energy corresponding to the same peak. We consider the present results as a prediction study for those compounds. We hope that our present work will stimulate some other works on these materials.

4. Conclusion

To conclude, a more detailed first-principles calculation was carried out for the study of the electronic structure, magnetic and linear optical properties of the Fe_2VAI and Fe_3Al by using the FPLAPW method. It was found that the lattice constant and spin magnetic moments with the GGA method differ more from the respective experimental values than those calculated with the LSDA method for Fe_3Al . Furthermore, our calculated lattice constant and spin magnetic moments with the LSDA method are in overall better agreement with experiment for

Fe₃Al. Our results show that Fe₂VAl are nonmagnetic. This is consistent with other theoretical and experimental results. In contrast to recent experimental data, our calculations are in good agreement with experimental reflectivity spectra. On the other hand, the contributions of various transitions peaks are analyzed from the imaginary part of the dielectric function.

Acknowledgements

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