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Electronic structures and optical and magneto-optical properties of RFe_2 ($R = Y$ and Lu) intermetallic compounds

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Abstract. The electronic structures of RFe_2 ($R = Y$ and Lu) were calculated using the linear-muffin-tin-orbitals method within the local-spin-density approximation. For $LuFe_2$ the 4f electrons were treated as band electrons. The calculated band structures and densities of states were similar to those of previous publications. The calculated magnetic moments were also in good agreement with both previous calculations and experiments. The diagonal and off-diagonal components of the optical conductivity tensor were calculated, including the dipole transition matrix elements. The self-energy corrections to the calculated optical conductivity spectra led to a reasonable agreement between experiments and the theoretical calculations for both components. The most significant contributions are from the regions near the Γ -L and Γ -X lines; in particular the regions near the Γ and L points make especially large contributions. The bands involved in the 2 eV shoulder in the measured optical conductivity spectrum are either p-d hybridized (occupied) ones or ones with mostly d character (unoccupied).

1. Introduction

The intermetallic compounds of rare earths (R) with transition metals (M) have been studied intensively because of their unique magnetic properties and technological importance [1]. If $M = Fe, Co$ or Ni there are two sources of magnetism: one is the M 3d and R 5d electrons, whose magnetism can be described by the band theory, and the other is the localized 4f electrons, which can be successfully described by the Russell–Saunders scheme [2].

The optical and magneto-optical properties of Laves phase RFe_2 have been measured several times [3–6]. Sharipov *et al* [3] measured the optical conductivity spectra and the magneto-optical equatorial Kerr effects of RFe_2 ($R = Gd, Tb, Dy, Ho, Er$), YFe_2 and Y_2Fe_{17} . They argued that the differences between the magneto-optical spectra are due to the 4f electrons. Their argument was based on the fact that the optical conductivity spectra of RFe_2 were similar to that of YFe_2 , but the magneto-optical spectra are different from each other.

A meaningful interpretation of the optical properties of solids strongly depends on the theoretical calculations of the electronic band structures. There are several band-structure calculations available [2, 7–9], treating the 4f electrons as an outer core. Which method provides a proper treatment of the electrons in an unfilled f shell is still controversial. Since the first spin-polarized band-structure calculation of Gd [10], the 4f electrons have been treated as an outer core in many band-structure calculations. Brooks and co-workers calculated the electronic structures of RFe_2 ($R = Gd$ – Lu) [2, 9] and concluded that the 4f

spin density can be treated as a part of an outer core during the self-consistent calculations. However, this conclusion is still questionable, because the calculations were mainly related to magnetic properties and, although the results successfully reproduced the measured magnetic moments and the Russell–Saunders scheme can give a correct 4f magnetism, they could not completely resolve the puzzle of the 4f electrons.

In this work we present the results of electronic band-structure calculations of YFe_2 and LuFe_2 using the tight-binding linear-muffin-tin-orbitals (TB-LMTO) method. The calculated magnetic moments are close to those of the previous calculations [7, 9] as well as the experimental values. While the inclusion of spin–orbit coupling does not affect the calculated magnetic moments significantly, it is very important in the optical conductivity calculations, especially as regards the magneto-optical spectra. Because of the difficulty of carrying out a proper treatment of 4f electrons in the electronic structure calculations and the similarity of the optical conductivity spectrum of RFe_2 to that of YFe_2 , we chose to calculate the electronic structures and the optical conductivity spectra of YFe_2 and LuFe_2 . Since Y and Lu have completely empty and completely filled 4f orbitals, respectively, the calculational results will give a relatively simple but still meaningful insight into the underlying physics of RFe_2 compounds.

This paper is organized as follows. In section 2 the details of the theoretical calculations are presented. In section 3 the results and a discussion are given. Finally, section 4 will conclude this paper.

2. Theoretical calculations

The band structures were calculated using a scalar-relativistic version of the TB-LMTO method using the atomic-sphere-approximation (ASA) within the local-spin-density approximation (LSDA). We chose the magnetization to lie along the z -axis direction. We also calculated the electronic structure for YFe_2 with the magnetization in the (111) direction, because the easy direction of magnetization for YFe_2 is the (111) direction [11]. However, the results are almost identical to those for the case of the magnetization lying along the z -axis direction.

Since the spin–orbit coupling is important to the magneto-optical effects [12], it is also included during the self-consistent calculations. The crystal symmetries of the compounds are reduced to tetragonal in the spin-polarized band-structure calculations. Consequently, the irreducible wedge of the Brillouin zone (BZ) is 1/16 of the whole reciprocal unit cell. In generating the self-consistent one-electron potential, the whole reciprocal unit cell was divided into $8 \times 8 \times 8$ parallelepipeds.

Once the self-consistent potential and charge were produced, the whole reciprocal unit cell was divided into $20 \times 20 \times 20$ parallelepipeds, and the energy eigenvalues and eigenfunctions were calculated at every corner of the parallelepipeds to calculate the density of states (DOS) and the optical conductivity and magneto-optical spectra. The eigenfunctions are used in the calculation of the dipole transition matrix elements in the optical conductivity $\sigma(\omega)$ given by

$$\sigma(\omega) = \frac{\pi e^2}{3m^2\omega} \sum_{f,i} \int_{BZ} d^3k \frac{2}{(2\pi)^3} |\mathbf{P}_{fi}|^2 \delta[E_f(\mathbf{k}) - E_i(\mathbf{k}) - \hbar\omega]$$

where

$$\mathbf{P}_{fi} = \frac{\hbar}{i} \langle f | \nabla | i \rangle$$

where m and e are the electronic mass and charge, respectively, $\hbar\omega$ is the incident photon energy, $E_i(\mathbf{k})$ and $E_f(\mathbf{k})$ are the energies of the initial and final states, respectively, and \mathbf{k} is the wave vector inside the BZ where the transition $E_i(\mathbf{k}) \rightarrow E_f(\mathbf{k})$ occurs. Each parallelepiped was further cut into six tetrahedra and the BZ integration was performed by the linear-energy-tetrahedron method [13]. For $LuFe_2$ the 4f electrons were treated as band electrons in the self-consistent calculations, and this did not give significantly different results from the electronic structures obtained with the 4f electrons treated as an outer core.

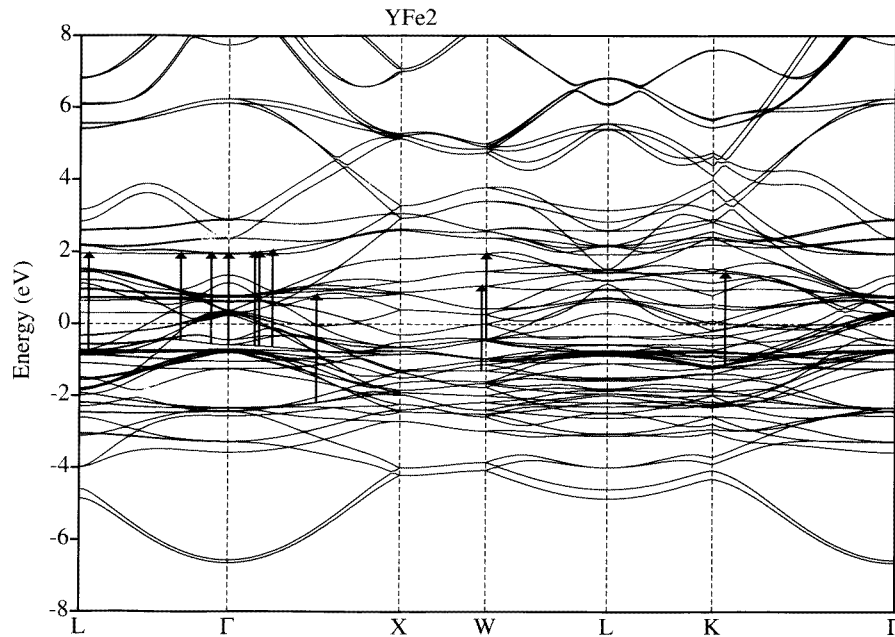


Figure 1. The band structure of YFe_2 along some high-symmetry lines. Strong interband transitions corresponding to the 2.0 eV shoulder are denoted by arrows.

3. Results and discussion

The lattice constants used in the band-structure calculations are 13.91 au for YFe_2 and 13.64 au for $LuFe_2$. The radius of the Fe muffin-tin sphere was 2.70 au for $LuFe_2$ and 2.76 au for YFe_2 . It was 3.38 au for Y and 3.31 au for Lu. The resultant band structure is shown in figure 1. The calculated band structures of the two compounds are very similar to each other, except that there are occupied 4f bands of $LuFe_2$ about 4 eV below the Fermi level. For $LuFe_2$, the bands above the Fermi level have slightly higher energy than those of YFe_2 . The positions of the Fermi level are also very similar in the two cases. This can be understood if we notice that the 4f electrons are localized in their atomic volume and, therefore, form very narrow and flat bands in the E - \mathbf{k} diagram. This means that the presence of the 4f electrons does not significantly modify the band structure away from the position of the 4f bands.

The calculated DOS curves are very similar to those of the previous calculations; however, the DOS at the Fermi level, $N(E_F)$, differs. $N(E_F)$ takes the values 50.0 states $Ryd^{-1}/f.u.$ for YFe_2 (32.5 states $Ryd^{-1}/f.u.$ in reference [7]) and 41.2

states $\text{Ryd}^{-1}/\text{f.u.}$ for LuFe_2 (157.6 states $\text{Ryd}^{-1}/\text{f.u.}$ in reference [9] for the paramagnetic case).

The calculated magnetic moment is $2.83 \mu_B/\text{f.u.}$ for YFe_2 ($2.72 \mu_B/\text{f.u.}$ in reference [7]) and $2.80 \mu_B/\text{f.u.}$ for LuFe_2 ($2.67 \mu_B/\text{f.u.}$ in reference [9]); these values are similar to the measured ones ($2.90 \mu_B/\text{f.u.}$ for YFe_2 [14, 15] and $2.85 \mu_B/\text{f.u.}$ [16] or $2.93 \mu_B/\text{f.u.}$ [17] for LuFe_2). As shown in references [7] and [9], Y and Lu also have small but non-negligible magnetic moments aligned antiparallel to the Fe moments. Y has a moment of $0.45 \mu_B$ and Lu a moment of $0.37 \mu_B$.

We also calculated the electronic structures without including the spin-orbit interactions and found that they do not significantly affect the theoretical values of the magnetic moments and the DOS; however, the calculated optical conductivity spectrum is sensitive to the spin-orbit interactions.

The calculated optical properties of rare-earth metals and their compounds, obtained treating 4f electrons as among the band electrons, usually did not agree well with the experiments [18], and the 4f electrons are known to contribute very little to the optical conductivity in the infrared-visible-ultraviolet (IR-vis-UV) energy range due to the large Coulomb repulsion between f electrons, which is caused by the large angular momentum of the 4f electron [19]. If we treat the electrons in a partially filled 4f shell as band-like, the 4f bands appear near the Fermi level and hybridized with the other bands, resulting possibly in incorrect electronic structures around the Fermi level. Furthermore, the optical conductivity spectra of RFe_2 ($\text{R} = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er) compound spectra are very similar to each other [3]. Therefore, the calculated optical conductivity spectra of YFe_2 (empty 4f shells) and LuFe_2 (filled 4f shells)—for which we do not need to worry about whether the 4f electrons can be treated as band electrons or only as an outer core—will give meaningful information relating to the interpretation of the measured spectra of RFe_2 compounds.

Since the calculations are usually done for the zero-temperature ground state, the calculated optical conductivity spectra have many sharp peaks and fine structures which can hardly be observed in measurements because of lifetime-dependent broadening effects and because the instrumental resolution also smears out many fine features. To simulate these effects, we used Lorentzian lifetime broadening with an energy-dependent broadening factor [20]. The broadened spectra are shown in figure 2. Although the two spectra closely resemble each other in both shape and magnitude, the position of the prominent structure is different from that for the measured ones [3]. Measurements showed a shoulder which has a plateau at around 1.8–2.3 eV, while the calculations showed a similar structure at around 2–3 eV. In order to correct this discrepancy, we applied the self-energy correction given by

$$\hat{\sigma}(\hat{\omega}) = \frac{1}{1 + \lambda} \sigma\left(\frac{\omega}{1 + \lambda}\right)$$

which is successfully used for many transition metals and their compounds [21]. This self-energy correction accounts for the effect of changing the excited-state energies $\hat{E}_n(\mathbf{k})$ relative to the energies, $E_n(\mathbf{k})$, calculated from the ground-state potential, given by [22]

$$\hat{E}_n(\mathbf{k}) = E_n(\mathbf{k}) + \lambda[E_n(\mathbf{k}) - E_F].$$

Although the parameter λ is dependent on the band index n and the wave vector \mathbf{k} , we assumed it to be constant. $\lambda = -0.12$ can for both compounds shift the shoulder in the calculated spectrum to that of the measured one. The negative value of λ is not unusual, especially for transition metals and their compounds. For instance, $\lambda = -0.18$ for Ni_3Al [21], $\lambda = -0.15$ for CoAl [23] and $\lambda = -0.12$ for Ni [24]. The self-energy-corrected spectra are also shown in figure 2.

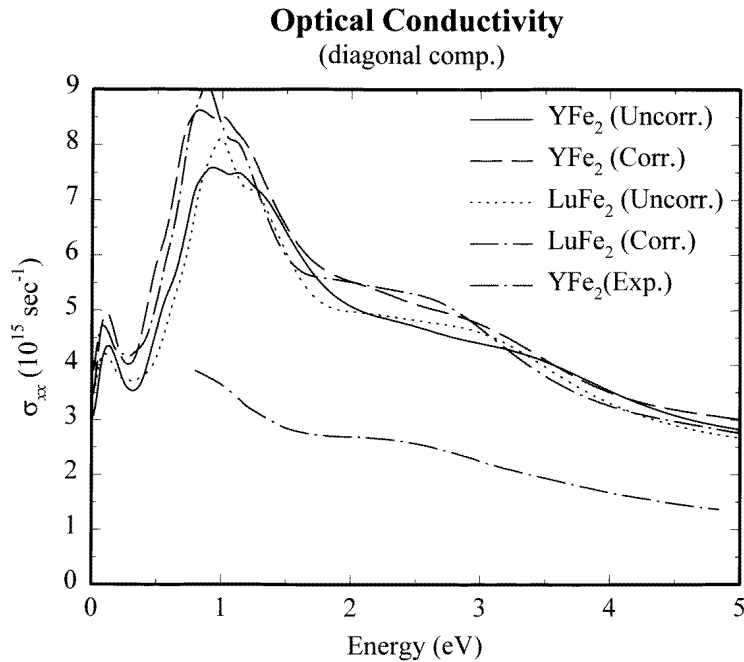


Figure 2. Calculated optical conductivity spectra of YFe_2 (solid line) and $LuFe_2$ (dotted line). The self-energy-corrected spectra are also included (the dashed line for YFe_2 and the chain line for $LuFe_2$). Experimental data digitized from reference [3] are also shown.

The magnitudes of the corrected optical conductivity around 2.0 eV are about twice as large as those of reference [3]. The samples used in reference [3] are polycrystalline ones. The method of sample surface treatment of reference [3] may cause a reduction of the magnitude of the measured spectrum. The authors used $1 \mu\text{m}$ diamond powder for the final stage of mechanical polishing and chemically polished the sample to remove the damaged layer of the mechanically polished surface. However, as pointed out in reference [21], the $1 \mu\text{m}$ diamond powder used for the final polishing causes more damage to the surface than $0.05 \mu\text{m}$ alumina powder and, during the chemical polishing, the polishing chemicals may attack the sample surface unevenly, leaving a wavy surface. The chemical polishing also leaves a chemical overlayer which may or may not be transparent in the energy range for which the measurements were made. Both the macroscopic wavy surface and the chemical overlayer may reduce the magnitude of the measured optical conductivity spectra. Even a careful mechanical polishing with a finer grade of polishing powder for the final stage of polishing could easily increase the magnitude of the optical conductivity by $\sim 20\text{--}30\%$ [21, 25] or $45\text{--}50\%$ [26]. However, we should be cautious when interpreting the difference between the experiment and the calculation, because the calculation is only an approximation. This means that we should consider the fact that the magnitude obtained from the theory is larger than that obtained from the experiment as an indication of improvement being needed in the measurement technique.

The surface damaged due to mechanical polishing may be recrystallized by a light annealing at $\sim 100^\circ\text{C}$ and this may increase the magnitude of the optical conductivity by $\sim 15\text{--}20\%$ [25]. Therefore the differences between the magnitudes of the measured and calculated spectra may be substantially reduced by using a high-quality single crystal and

an appropriate surface treatment such as a careful mechanical polishing using a finer grade of polishing agent in the final stage, followed by an annealing to regain the crystal structure of the damaged surface.

To obtain a deeper understanding of the origin of the 2.0 eV shoulder we need to know which k -points and band pairs contribute significantly to this structure, and the characteristics of the band pairs. In order to get this information we should set an energy window appropriately chosen to fit the features of the optical conductivity spectra during calculations and, if the energy difference between two energy levels in the same tetrahedron, for which the optical transition is allowed, falls into this window, the k -point, the indices of the band pair and the optical conductivity contributed by the tetrahedron should be stored in a separate file, which will be used for later analysis.

Density of states (YFe₂)

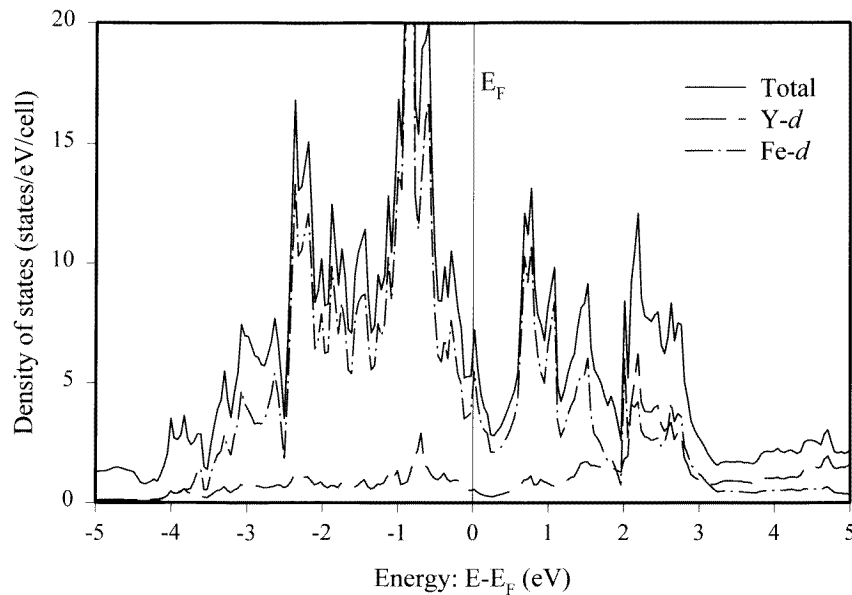


Figure 3. The total DOS (solid line) and the Y (dashed line) and Fe (chain line) 3d partial DOS.

For YFe₂ the most prominent contributions to the 2.0 eV shoulder, corresponding to the 2.5 eV shoulder in the theoretical spectrum without the self-energy correction, are from the region near the Γ -L and Γ -X lines (27–30 \rightarrow 53–56). The occupied bands are located 0.6–0.8 eV below the Fermi level and the unoccupied ones 1.9–2.1 eV above it. Both groups of bands disperse very little. This is characteristic of localized d bands, making sharp peaks in the DOS. Hence, these groups of bands are parallel to each other, resulting in there being sharp peaks in the joint density of states and a large optical conductivity in spite of the small transition matrix element. The lower bands have predominantly Fe 3d character hybridized with p bands, while the upper bands have mostly d character, which is a mixture of Fe 3d and Y 3d or Lu 5d character (see figure 3). The character of the upper bands is mixed due to the hybridization between the bands, and the hybridization causes the Lu 5d magnetic moment to align antiparallel to the Fe 3d moments [9].

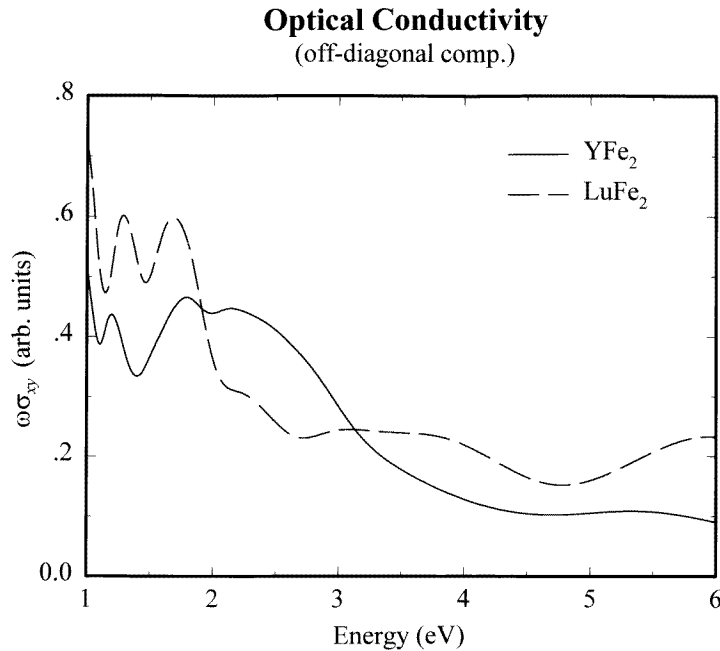


Figure 4. The self-energy-corrected theoretical $\omega\sigma'_{xy}$ -spectrum of YFe_2 (solid line) and $LuFe_2$ (dashed line).

Besides these transitions, there are three other strong transitions: (i) nearly half way between the Γ and X points ($12 \rightarrow 43$), (ii) near the W point ($35 \rightarrow 50$) and (iii) near the K point, $\frac{9}{10}$ of the way from the Γ point ($25 \rightarrow 46$). These transitions also have similar band characters to that of the aforementioned strong transitions.

For $LuFe_2$, the situations are very similar to those for YFe_2 , except as regards the latter three transitions, which is not significant in the calculated optical conductivity spectrum of $LuFe_2$.

We also calculated the absorptive part of the off-diagonal components of the optical conductivity tensor, which is closely related to the magneto-optical spectrum. In reference [3] the measured $\omega\sigma'_{xy}$ -spectrum has a local maximum at around 2 eV and a broad local minimum at around 3.5 eV. Our calculated spectra have similar features. As shown in figure 4, both spectra have a local maximum at around 2 eV and a broad local minimum at around 4.6 eV for YFe_2 , and a local minimum at around 3 eV for $LuFe_2$. For YFe_2 the high-energy feature occurs about 1 eV higher in the calculated spectrum than in the experimental one. Since the measured spectrum is given in arbitrary units for $\omega\sigma'_{xy}$, it is not possible to compare the calculated spectrum with the measured one quantitatively.

4. Conclusions

The ASA TB-LMTO band calculations successfully reproduce the magnetic moments of YFe_2 and $LuFe_2$. In these compounds the 4f electrons do not play a significant role, as expected. The optical conductivity spectra of YFe_2 and $LuFe_2$ were calculated. The self-energy corrections, both real (position shifts of structures in the optical conductivity spectra) and imaginary (broadening), markedly improve the agreement between experiment

and calculations.

The origin of 2.0 eV shoulder was clarified by using information about which tetrahedra and band pairs contribute significantly to the structure. Most contributions are from the regions near the Γ -L and Γ -X lines; the regions near the Γ and L points make the main contributions. The angular momentum characteristics of the band pairs involved in these transitions are either p-d hybridized (occupied) ones or ones with hybridization between Fe 3d and Y 3d or Lu 5d bands.

Since the measured optical conductivity spectra of RFe₂ (R = rare earth) exhibit very similar shapes [3], it is very important to understand the origin of the features in the IR-vis-UV region of the spectra, and further study of the compounds with the rare earths having partially filled f bands will give a more detailed understanding of the similarities of the optical conductivity spectra and the differences between the magneto-optical spectra. This will be the subject of a future publication.

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