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First-order metamagnetic transition in iron monosilicide

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Abstract. The influence of a high magnetic field on the band structure and optical conductivity of FeSi has been studied by the *ab initio* full-potential LMTO-PW and relativistic LMTO-ASA methods with an applied field included. It is found that the applied external magnetic field induces a metallic magnetic state through a first-order metamagnetic transition, i.e. at a critical magnetic field of about $H_{cr} = 170$ T there is a large steplike increase in the calculated magnetization, with a magnetic moment of 0.7 μ_B. The magnetized state persists while the field is gradually reduced from above the metamagnetic transition (a hysteresis effect). The calculated optical conductivity (OC) at the critical field H_{cr} differs substantially from the zero-field OC in the infrared region.

1. Introduction

Silicides form an important group of transition metal compounds with interesting physical properties. While the majority of the silicides turn out to be metallic, some of them, including the B20 cubic phase of iron monosilicide, have been found to exhibit semiconducting properties [1]. The unusual temperature dependence of the magnetic susceptibility and the Curie–Weiss behaviour at room temperatures [2] have been attributed to the thermal electron activations across a narrow energy gap of about 0.05 eV [3]. Moreover it was proposed [4] that the magnetic properties of FeSi can be explained by use of a self-consistent renormalization theory of spin fluctuations for a nearly ferromagnetic semiconductor. The predicted temperature-induced local moments in FeSi were observed by means of neutron paramagnetic scattering [5]. However, Aeppli and Fisk [6] recently suggested that FeSi may be a Kondo insulator; these require a strong hybridization at the Fermi level between d and s, p states.

One of the unresolved problems is a strange effect of the negative magnetoresistance at low temperature and magnetic field around 3 T [7]. In [7] the authors concluded that

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the possibility of Anderson localization being the origin of the negative magnetoresistance should be considered.

Recently [8] we reported results on the influence of high magnetic field and pressure on the band structure of iron monosilicide. It was found that applied magnetic fields induce a transition from the ground-state semiconducting paramagnetic phase to the metallic ferromagnetic one. This first-order metamagnetic transition occurs at a critical field (H_{cr}) of about 170 T. It should be noted that this result was obtained under an applied magnetic field which was increased gradually in small steps of 0.25 mRyd, or 30 T. Also note that in the recent paper [9] the authors predicted a first-order transition in an external magnetic field to a metallic ferromagnet with a net magnetic moment of 4 μ_B/cell. They used the LDA + U fixed-spin-moment scheme that takes into account the additional local Coulomb interactions, and have found that H_{cr} is very sensitive to the choice of U. From their results it follows that H_{cr} will be around 3500 T provided that $U = 0$, i.e. in conventional LSDA methods.

It is interesting to consider what will happen if we gradually decrease the magnetic field after having reached H_{cr}. Theory [10] predicts a strong hysteresis effect of the magnetization (m) which arises from *tunnelling* if the total energy of an electron system has the double-minima feature, one minimum being at the ground state and the second minimum being at a finite value of m.

In this paper we have used another calculational scheme, more accurate than those in [8] and [11], and extended our consideration to an analysis of the hysteresis properties and the optical spectrum in the metamagnetic state. The purpose of this paper is to present our study of the first-order metamagnetic transition in FeSi under a high magnetic field, the hysteresis effect found, and the changes in the calculated optical conductivity near the transition point.

2. Method of calculation

The electronic structure calculations for iron monosilicide have been performed by using the *ab initio* full-potential linear muffin-tin orbitals (FPLMTO) method [12, 13] with plane-wave expansions for the LMTOs in the interstitial region. Exchange and correlation contributions to the crystal potential have been included through the von Barth–Hedin local spin-density approximation (LSDA) [14]. Here we consider what electronic changes occur as the external magnetic field is imposed in both regimes, i.e. with the field increase and with the field decrease.

To study the influence of high magnetic fields on electron states in FeSi, we have performed a set of constrained LSDA calculations at the experimental equilibrium volume. For a given applied magnetic field, the potentials of majority and minority electrons are split by the field energy ($\mu_B H$) throughout the iterations until the total energy (and the spin magnetic moment, m) develops self-consistently. In other words, the magnetic field is fixed and the spin magnetic moment is allowed to float until the total energy is minimized; thus m is obtained as a function of H. The FPLMTO technique is well suited to such types of problem because we generate the electronic structure, and charge- and spin-density distributions of compounds in a completely unified way, i.e. without any prior assumptions or adjustable parameters.

In the FPLMTO method the space is divided into the touching MT spheres (R_{MT}) surrounding each atom and the remaining interstitial region (Ω_{int}). Within the MT spheres the wave functions are represented in terms of numerical solutions of the radial Schrödinger equation for the spherical part of the potential multiplied by spherical harmonics as well

as their energy derivatives taken at a certain fixed set of energies E_ν. In the interstitial region, the wave functions are spherical waves—namely the Hankel functions, taken as the solutions of the Helmholtz equation with a certain fixed value of the average kinetic energy $E = \kappa_\nu^2$.

We use the double-κ spd LMTO basis set (18 orbitals per atom) with one-centre expansions inside the MT spheres performed up to $l_{\max} = 6$. In the interstitial region, the s, p, and d basis functions are expanded in plane waves up to 17.6, 25.2, 36.8 Ryd (750, 1356, 2324 PWs) for Fe, and up to 14.3, 20.4, 30.7 Ryd (586, 1020, 1790 PWs) for Si. The charge densities and the potentials are represented inside the MT spheres by spherical harmonics up to $l_{\max} = 6$, and by plane waves with a 123.5 Ryd energy cut-off (14 146 PWs) in the interstitial region, which corresponds to the (32, 32, 32) fast-Fourier-transform grid in the unit cell.

For complex crystal structures it is important to control and manage the process of stabilization of the self-consistent iterations, because providing good band-structure computations in the actual crystal structure B20 is obviously important for the details of the electronic structure, and reliable densities of states and spin magnetic moments. With this aim, the Broyden procedure [15] for mixing input and output electron and spin densities has been applied. Earlier we found out [8] that the use of this scheme significantly accelerates charge- and spin-density convergence. The latter was checked through the total energy, which was stable better than 0.1 μRyd in the final iterations towards self-consistency.

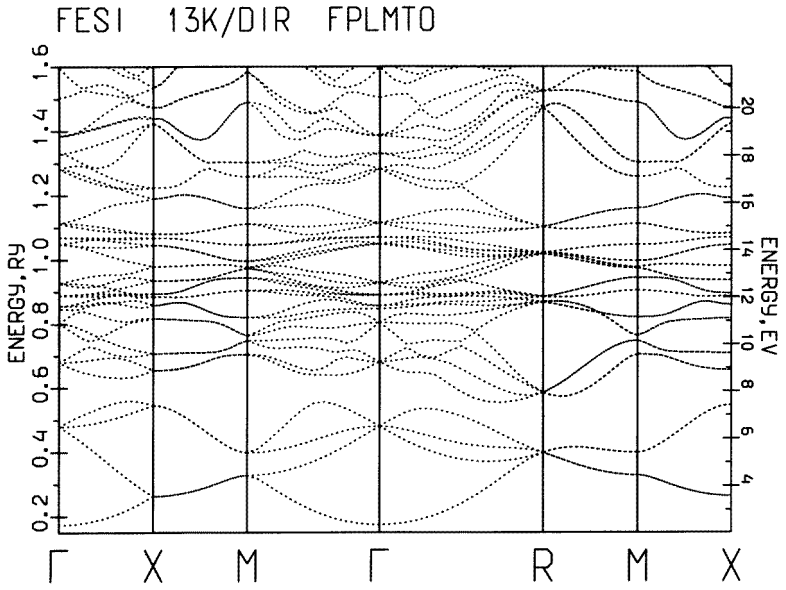


Figure 1. The band structure of FeSi along the high-symmetry directions of the B20 simple cubic Brillouin zone.

The ***k***-space Brillouin zone integrations needed for constructing the charge densities and the potentials are performed over the (13, 13, 13) grid (195 points per 1/24 irreducible part of the B20 simple cubic Brillouin zone) by use of the improved technique developed in [16]. The MT-sphere radius of Fe is taken to be 2.064 au and the radius of the silicon sphere is 2.270 au. FeSi crystallizes in a simple cubic structure with four Fe atoms and four Si atoms in a unit cell with the following coordinates (4a): (xxx), $(1/2 + x, 1/2 - x, \bar{x})$, $(\bar{x}, 1/2 +$

$x, 1/2-x)$, and $(1/2-x, x, 1/2+x)$. The space group is $P2_13$ (T^4) and the overall point symmetry is tetrahedral. The local symmetry of the Fe atom is trigonal, there being one Si nearest neighbour, three Si second neighbours, and three Si third neighbours. We did not perform a minimization of the total energy with respect to the volume and the internal atom position parameters x_{Fe} and x_{Si}. Instead, we have used the experimental lattice constant, $a = 8.483$ au (4.489 Å), and the internal parameters $x_{Fe} = 0.137a$ and $x_{Si} = 0.842a$ [17].

Our calculations of optical spectra are based on the widely used RPA-type expression for the interband absorptive part of the conductivity tensor (see, for example, reference [18]). The intraband part of the diagonal components has been calculated by use of the Drude formula. Optical calculations have been carried out by the relativistic linear muffin-tin orbital (RLMTO-ASA) method [12, 18] including spin–orbit coupling (SOC) in the variational procedure which implies that the SOC Hamiltonian is diagonalized using the spin-polarized semirelativistic wave functions as a basis set. We used the grid of 204 $\boldsymbol{k}$-points in the 1/24 irreducible part of the simple cubic Brillouin zone, whereas the basis functions were s, p, d, and f LMTOs for the Fe atom and s, p, and d LMTOs for the Si atom. The ratio of ASA radii is taken as $S(\mathrm{Fe})/S(\mathrm{Si}) = 0.9$. This choice has provided charge transfer between the Fe and Si sites equal to $0.2e$. In addition, we smooth the calculated optical conductivity with the linear inverse lifetime $\Gamma(\omega) = 0.1E$ eV.

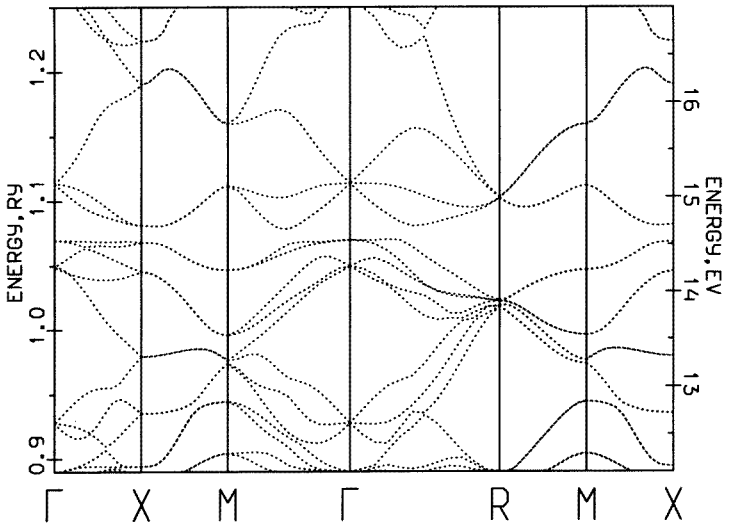


Figure 2. An expanded plot of the FeSi band structure (figure 1) near E_F.

3. Results and discussion

Figures 1 and 2 show the calculated FPLMTO-PW energy bands along high-symmetry lines of the B20 simple cubic Brillouin zone (BZ). The present semirelativistic LSDA calculations, like the others [19–21], find a narrow indirect gap in the spectrum of size 0.04 eV, the lowest direct transitions (the direct gap located at the X point of the BZ) being at 0.16 eV. The indirect gap is formed by the top of the valence band along the ΓR direction and the bottom of the conduction band along the ΓM direction. The Fermi level lies inside the indirect gap and occurs in the middle part of the Fe 3d states. 24 bands below E_F are fully filled

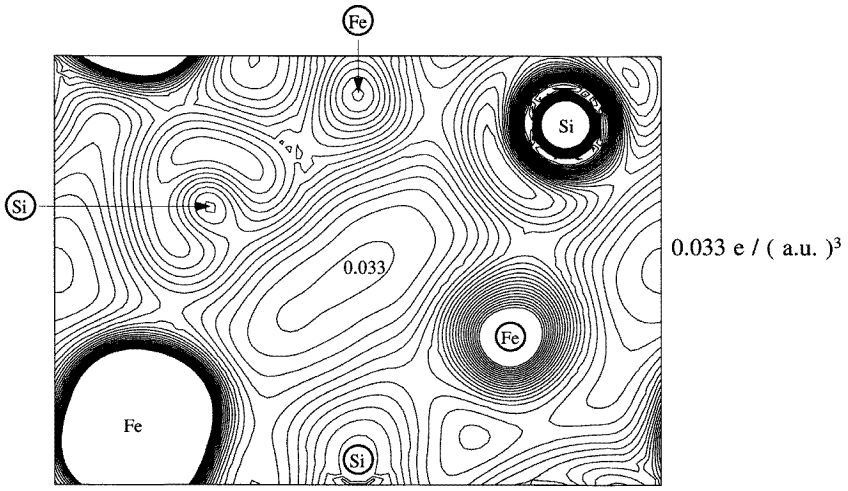
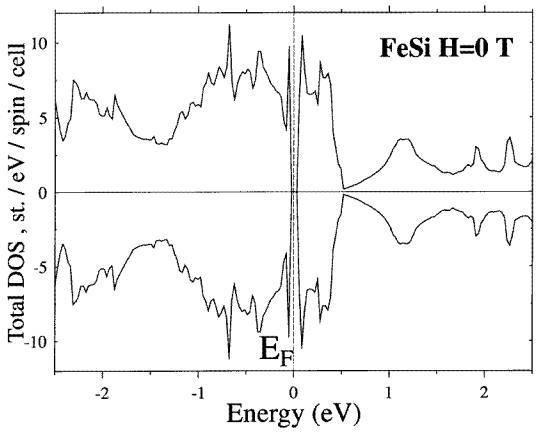


Figure 3. A contour map of the charge density in the (110) plane for FeSi. The vertical direction is parallel to the [001] axis. Equicharge contours are plotted with steps of $0.003e$ au^{-3}. Symbols in bold circles denote the projections of nearest atoms which are out of the (110) plane.

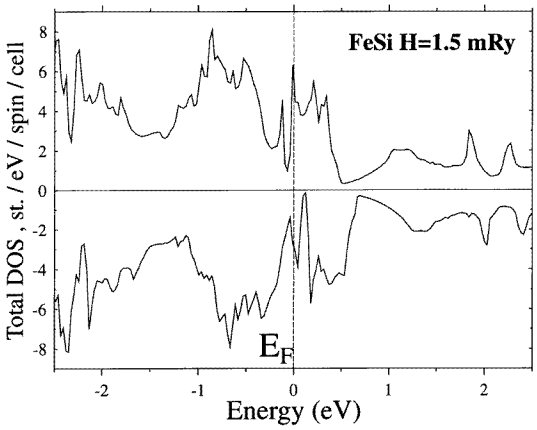
and contain 48 valence electrons per unit cell. The lowest four bands are composed from the Si 3s states. The bands above these cover the region of the Fe 3d–Si 3p hybridization. This region spans up to the Fermi level. Comparison of our FPLMTO-PW results with the LAPW calculations for FeSi [19] shows very good agreement. This raises our hopes, since we are going to study small perturbations of the band structure by applying an external magnetic field, the value of which is comparable with the energy gap in FeSi.

In FeSi the interstitial region occupies 44% of the unit-cell volume and the B20 structure will be considered as 'open'. Usually, to increase the accuracy of the calculations, additional 'empty' muffin-tin spheres are included in the open regions of the unit cell [21]. However, the FPLMTO-PW method [13] represents the charge density and potential as a plane-wave expansion in the interstitial region. This is a very accurate program, which does not need 'empty' spheres, and can work, in principle, with any low-symmetry structures. It is necessary just to increase the number of plane waves. Figure 3 shows a contour plot of the charge density in the (110) plane. The diagonals of the rectangle are the [111] directions. The plane crosses only one Fe atom and one Si atom. It is seen that the charge density in the interstitial region is far from the spherically symmetric one, and reflects a very complex spatial distribution.

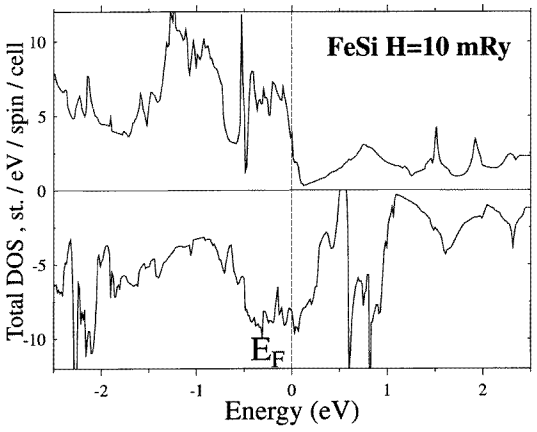
Returning to the main topic of this paper, consider the influence of the applied magnetic field on the electronic structure of FeSi. The results of our *ab initio* LSDA + field calculations are shown in figure 4. The zero-field DOS function (figure 4(a)) is in good agreement with our relativistic DOS at $H = 0$ T [11]. Figure 4(b) shows the DOS at the magnetic field $H = 1.5$ mRyd (about 176 T). It is seen that under the high magnetic field there is a transition from the non-magnetic semiconducting state (figure 4(a)) to the metallic ferrimagnetic one, the magnetic moments on the Fe and Si sites being oriented antiparallel to each other, with values of $+0.198\ \mu_B$ and $-0.012\ \mu_B$, respectively. The total magnetic moment per unit cell at this magnetic field is equal to $0.741\ \mu_B$. Such an orientation of the local magnetic moments at Fe and Si sites proves that a simple rigid-band-shift model would be unreliable for the description of the induced magnetic state in FeSi.



(a)



(b)



(c)

Figure 4. Total densities of states near the Fermi level (E_F) for the spin-up (upper panel) and spin-down (lower panel) electrons in FeSi: (a) at $H = 0$ T, (b) at $H = 1.5$ mRyd, and (c) at $H = 10$ mRyd. The energies are given with respect to E_F.

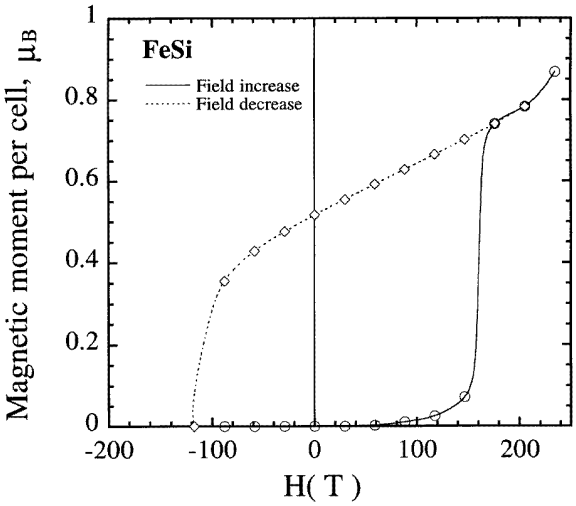


Figure 5. The field dependence of the calculated magnetic moment in FeSi. Circles connected by a solid line denote the field increase in steps of about 30 T, and diamonds connected by a dashed line denote the field decrease starting from 200 T in steps of the same size.

Figure 5 shows the calculated field dependence of the spin magnetic moment $m(H) = n_\uparrow(E_F, H) - n_\downarrow(E_F, H)$, where the n_σ ($\sigma = \uparrow, \downarrow$) are the spin-up and spin-down numbers of states at E_F. First, consider the field-increase regime (circles connected by a solid line). m is approximately linear at low magnetic fields up to $H \approx 100$ T and very small, which is in accordance with experimental observations of the magnetization in magnetic fields up to 5 T [22], and then there is a steep increase at $H_{cr} \approx 170$ T. Such almost steplike behaviour in $m(H)$ indicates the onset of the metamagnetic phase transition.

From the DOS curve obtained near the critical field (figure 4(b)), it is seen that the Fermi level falls in the region of sharp DOS changes for spin-up electrons, whereas for spin-down electrons the DOS near E_F is smooth. Hence, a large $\delta n_\uparrow(H \approx H_{cr})$ is responsible for large changes of $\delta m(H \approx H_{cr})$. This may be the origin of the 'computer-simulated' metamagnetic transition in iron monosilicide.

The field-decrease regime (diamonds connected by a dashed line in figure 5) demonstrates an interesting feature. Starting with the magnetized state *above* the metamagnetic transition at $H = 200$ T, and gradually *decreasing* the strength of the imposed magnetic field in small steps of about 30 T, our results show a hysteresis effect, i.e. an electron system does not return to the preceding spinless and low-spin states but sustains the net magnetization even at zero field. It should be noted that the system is theoretically capable of sustaining a magnetic moment even with a negative magnetic field (i.e. one that is opposite to the direction of magnetization). At the second negative critical field of about -100 T, an abrupt collapse of the moment occurs. Also, note that decreasing the imposed magnetic field to zero *before* reaching the first positive critical field value merely returns the magnetic moment to the former value of $m = 0\ \mu_B$.

Such a large steplike increase in the magnetization at the critical magnetic field (a metamagnetic transition) with a net moment persisting after the imposed field has been reduced (the hysteresis effect) was theoretically predicted for the first time for Pd metal by Jarlborg and Freeman [23], and was observed by Adachi *et al* [24] for $Co(S_xSe_{1-x})_2$ and Vinokurova *et al* [25] for $FePt_3$. The concept of itinerant metamagnetism in high

magnetic fields was proposed by Wohlfarth and Rhodes [26]. Then Shimizu [27] extended the ideas and investigated theoretically the conditions for the occurrence of a metamagnetic transition. Its occurrence can be described in the framework of these theories on the basis of the double-minimum feature in the total energy: a first local minimum at $m = 0$ (the system is non-magnetic) and another one at a finite m. The corresponding $m(H)$ curve shows a metamagnetic behaviour. The appearance of hysteresis phenomena was cited by Wohlfarth [10] as evidence for a first-order magnetic process, and attributed as arising from *tunnelling* if the Landau expansion of the free energy has a second minimum at a finite value of m which is below that at $m = 0$. Our calculated dependence of the total energy on the magnetic moment $E_{\rm tot}(m)$ does exhibit a local minimum at $m = 0$ (ground state) and another minimum at a finite m-value (about 0.7 μ_B).

Recently Anisimov *et al* [9] have reported LDA + U fixed-spin-moment-calculations for FeSi. They predict a first-order transition from the singlet semiconductor to a ferromagnetic metal with the total moment of 4 μ_B/cell. That means that the Fe atom has a magnetic moment of about 1 μ_B. However, they did not find a stable solution with 0.7 μ_B/cell. We believe that the value of the critical magnetic field is very sensitive to the value of the indirect gap in FeSi. Note that various band-structure methods give different results for this value. To check our results, we performed LSDA + field calculations at huge fields up to 1200 T, and did find a solution with 3.84 μ_B/cell (1 μ_B/Fe and -0.04 μ_B/Si) at $H = 1170$ T (figure 4(c)).

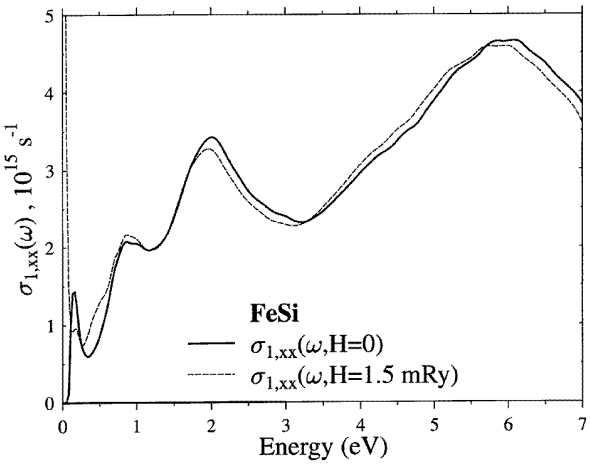
Finally, we calculated the optical response near the metamagnetic transition or, in other words, the optical conductivity of FeSi in the metallic ferromagnetic state. The RLMTO-ASA electronic structure and DOS curves obtained are similar to those for the FPLMTO-PW calculation except for details, as now we use the SOC contributions which remove the accidental band crossings inside the valence and conduction bands and the degeneracies due to the lowering of the crystal point symmetry. As a result of such modification of the band structure, the widths of the valence and conduction bands and the DOS at E_F slightly increase, and the value of the gap is reduced by half in comparison with the semirelativistic FPLMTO-PW band structure.

Figure 6(a) represents our calculated spectra $\sigma_{1,xx}(\omega)$, for $H = 0$ T [11] and $H \approx H_{cr}$. At zero field the absorption edge, which indicates the onset of the interband direct transitions where the OC starts to rise, is estimated as 0.046 eV.

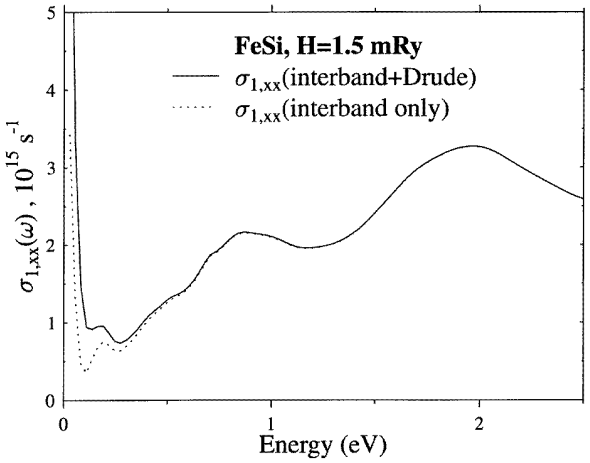
Note that our unsmoothed (ignoring any relaxation effects) $\varepsilon_{2,xx}(\omega)$ is in rather good agreement with the results of Fu *et al* (figure 1 in reference [20]) except for the position of main peak of $\varepsilon_{2,xx}(\omega)$. Our main peak is shifted downwards in energy by 0.06 eV compared to the semirelativistic data of reference [20]. At the critical field H_{cr}, the OC spectrum in the infrared region (0–1.5 eV) is considerably changed. Now the OC spectrum looks like a metallic one, and the interband transitions have their onset at negligible photon energies (figure 6(b)). From the calculated Fermi velocities $v_{F,x}$, the averaged Drude plasma frequency is equal to 1.46 eV.

4. Conclusion

We have performed a set of LSDA + field full-potential LMTO-PW calculations in order to clarify the influence of an external magnetic field on the electron states in iron monosilicide. The magnetic behaviour of FeSi can be understood in terms of the present calculated dependence of the total energy on the magnetization having a second local minimum at $m = 0.7$ μ_B which is below that at $m = 0$. At zero field, FeSi is a semiconductor and paramagnet. A slight increase of the imposed magnetic field (about 70 T) induces



(a)



(b)

Figure 6. (a) The optical conductivity of FeSi at $H = 0$ (solid line) and at the calculated critical field H_{cr} (dashed line), and (b) the only interband contribution (dotted line) to the optical conductivity at H_{cr} (solid line).

the transition to the metallic, low-spin magnetic state. Further field increase leads to the possibility of a metamagnetic transition at H_{cr}. The critical transition field H_{cr} is estimated from the calculated $m(H)$ dependence to be about 170 T. We have found a strong hysteresis effect of the magnetization with an applied field, in accordance with the theoretical predictions [10]. Decreasing the field to zero after having reached the critical value H_{cr} results in there being a finite moment even at $H = 0$ T. In FeSi, an electron system is capable of sustaining a magnetic moment even with negative (opposite to the direction of the magnetization) fields. At the negative field of about -100 T, an abrupt collapse of the magnetic moment occurs.

An important aspect of the first-order metamagnetic transition is the critical field needed to accomplish it. From our calculations at the experimental volume, H_{cr} is very large and is

estimated to be about 170 T. However, as there are magneto-volume effects involved in the first-order transition, a more realistic estimation would require a knowledge of the $H_{cr}(V)$ relation.

One further comment should be made. The value of the gap is significantly changed when the SOC is taken into account, as compared to that from a semirelativistic FPLMTO-PW calculation. It may be qualitatively assumed that in the relativistic FPLMTO-PW method the value of H_{cr} will be smaller than 170 T. Therefore, further investigations of the volume and SOC dependences of the metamagnetic transition could provide a basis for a better understanding of its origin.

At the critical field, the optical conductivity of FeSi in the infrared region (0–1.5 eV) is considerably changed compared to the zero-field OC. The high-field OC spectrum looks like a metallic one, and the interband transitions have their onset at negligible photon energies.

Acknowledgments

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