PHYSICAL REVIEW B VOLUME 49, NUMBER 3 15 JANUARY 1994-I

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Electronic structure and optical properties of FeSi, a strongly correlated insulator

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(Received 17 September 1993)

Kondo insulators are a class of materials with a nonmagnetic ground state characterized by extremely narrow charge-excitation gaps induced by strong electron correlations. Prompted by suggestions that FeSi may be strongly correlated in a similar class to the Kondo insulators, we present results for the electronic structure and optical properties for FeSi calculated with a self-consistent augmented spherical wave method. The calculated indirect gap ($\approx$ 0.1 eV) is roughly consistent with resistivity measurements which indicate a gap of about 50 meV. We calculate the optical response incorporating simple finite-temperature effects, namely, electron-phonon scattering of intrinsic carriers. We find that this provides a poor direct fit to recent infrared measurements. The number of intrinsic carriers is low compared to experimental observations, even with an *ad hoc* renormalization of the gap, and a strong scattering mechanism with attendant disordering of the band structure is required as well.

The unusual temperature dependence of the magnetic susceptibility of FeSi has provoked a great deal of interest for decades.[1,2] Moriya and others[3–5] have suggested that spin fluctuations cause the formation of a temperature-dependent localized magnetic moment which has subsequently been observed in neutron scattering.[2] With the renewed interest in other narrow-gap materials like $Ce_3Bi_4Pt_3$ and CeNiSn, in which the insulating gap is of order T_K, the Kondo temperature, FeSi merits reexamination to determine if it belongs to a new larger class of "strongly correlated insulators," which includes both rare-earth and transition-metal compounds. In contrast to the spin fluctuation picture, the Kondo insulator picture focuses on the character of the charge excitations at low temperature, where the system forms a nonmagnetic insulator with an extremely small gap. The insulating state is ascribed to a coherent hybridization gap, where the couplings have been modified by strong correlations and are characterized by a Kondo temperature scale T_K. With increasing temperature, the coherence is destroyed, and the behavior is similar to that of a dirty metal.

Recently, Schlesinger *et al.*[6] have measured FeSi's infrared reflectivity, and have observed an optical gap of 800 K which is essentially gone by 250 K, behavior which is reminiscent of that seen in neutron measurements of CeNiSn (Ref. 7) and $Ce_3Bi_4Pt_3$.[8]

In this paper we present results of an augmented spherical wave[9] (ASW) *ab initio* band-structure calculation for FeSi, including results for the optical conductivity. The ASW method has proven to be effective at calculating optical properties of other transition-metal silicides (e.g., $FeSi_2$ and $CrSi_2$),[10–12] reproducing the observed gap in $CrSi_2$ to within 15%. Based on early calculations on MnSi,[13] FeSi band-structure calculations were expected to predict semiconducting behavior. Thus by comparing the calculated optical response with experiment we hope to separate the features of the charge-excitation spectrum which are caused by strong correlation from those which are direct consequences of the electronic structure as estimated by the self-consistent local-density approximation (LDA) and hence attempt to identify features which relate to FeSi's correlated magnetic excitation spectrum.

In the ASW method,[9] the basis set consists of augmented spherical waves based upon muffin-tin potentials at the atomic sites. The scalar relativistic potentials are iterated to self-consistency by sampling over a 220-point irreducible wedge of the Brillouin zone, and incorporating exchange and correlation effects in the LDA. FeSi's crystal structure, $P2_13$,[14] consists of eight atoms per unit cell in a simple cubic lattice. Atoms are located at (u_i, u_i, u_i), $(u_i + \frac{1}{2}, \bar{u}_i + \frac{1}{2}, \bar{u}_i)$ and the points generated by a threefold symmetry about the (111) axis, for $u_{Fe} = 0.137$, $u_{Si} = 0.842$. As pointed out by Mattheiss and Hamann[15] this is a distortion of a rocksalt phase, where $u_{Fe} = 0.25$ and $u_{Si} = 0.75$. For our calculation we used a lattice

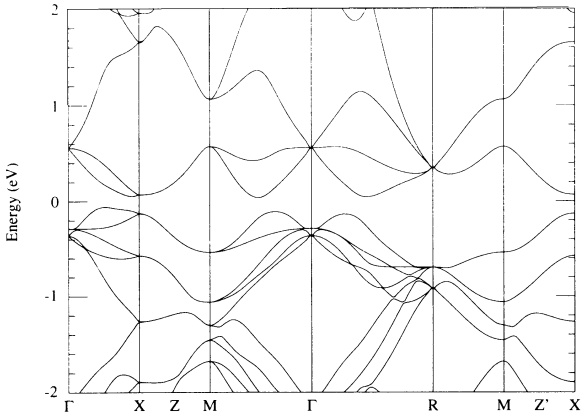

FIG. 1. Band structure of FeSi calculated using the ASW method near the Fermi energy. The Z and Z' symmetry lines are distinct due to the tetrahedral point symmetry.

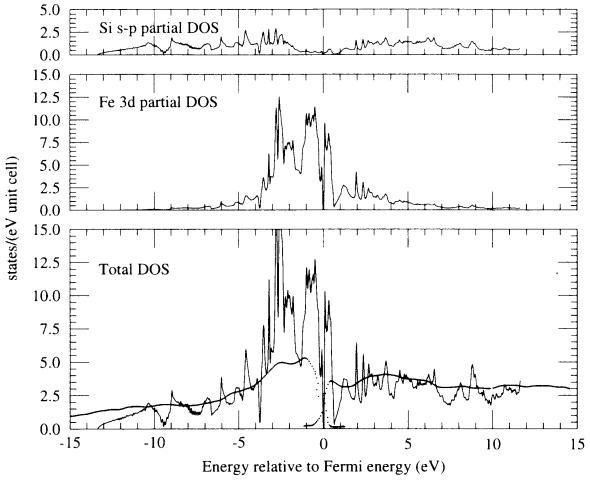

FIG. 2. ASW results for the total and partial DOS of FeSi with four formula units per cell. The DOS are calculated using nearly 3000 points in k space over an irreducible wedge of the Brillouin zone. Partial DOS reflect the muffin-tin ASW basis set. The total DOS is superimposed on x-ray photoelectron spectroscopy and bremsstrahlung isochromat spectroscopy results (Ref. 17) which are arbitrarily scaled with respect to each other and the calculation.

constant from x-ray diffraction measurements, $a = 4.489$ Å. Total energy calculations minimize the ground-state energy for a within 1% of the experimental value. We chose our atomic sphere radii to be equal and to fill the unit cell volume. Upon trying alternate values we found they caused little change in the details of the electronic structure—choosing $r_{\mathrm{Fe}}/r_{\mathrm{Si}} = 1.1$ changed the direct gap by about 1%. Spin-orbit effects, as well as relativistic corrections, were also found to have negligible effect on the structure.

Our calculation of the band structure (Fig. 1) exhibits an extremely narrow direct gap of 150 meV formed by $3d$ states from the iron atoms, and an indirect gap of ≈100 meV. This is consistent with the spin gap of 130 meV derived from fitting the temperature dependence of the magnetic susceptibility, $\chi(T)$, to a simple two-band model.[1] However, for this model the parameters which best fit $\chi(T)$ correspond to a two-band system with infinitesimal bandwidths (< 1 meV, far smaller than the d bands with widths of 0.5 eV). Our calculation is also supported by resistivity measurements which indicate a transport gap of about 50 meV.

Comparing our ASW results with recent linear augmented plane-wave (LAPW) calculations for FeSi (Ref. 15) and the earlier calculations for MnSi,[13] we find very good agreement, matching the magnitudes of the direct [0.15 eV vs 0.14 eV (Ref. 15)] and indirect band gaps (≈ 0.11 eV for both). However, the bands near the Fermi energy are in places shifted, differing by nearly 0.2 eV near Γ, which indicates some quantitative differences. Nonetheless, these discrepancies are smaller than those seen comparing calculations by Eppenga[10] and Christensen[16] in $FeSi_2$ where the ASW result for the indirect gap (≈ 0.4 eV) (Ref. 10) was smaller than the linear muffin-tin orbital value (≈ 0.8 eV).[16] Furthermore, near Γ the direct gap is rather large (≈ 0.8 eV) so the percentage difference is not so enormous.

This agreement between our calculation and that of Mattheiss and Hamann implies that the constraints of the ASW basis set should not be a hindrance for FeSi. This is fortunate, as we are interested in the region near the Fermi energy, where the density of states is quite large. The speed of the ASW method allows us to obtain a more detailed sampling of the Brillouin zone, for a more accurate sample of the density of states. Figure 2 illustrates the total and partial density of states (DOS), superimposed upon photoemission and inverse photoemission data of Oh, Allen, and Lawrence.[17] The larger features in the calculated DOS are clearly identifiable in the experimental data, which has not been corrected for background. As noted earlier,[17] the $3d$ valence band is somewhat narrower in the observations.

An important feature of the projected densities of states (Fig. 2) is that the bands close to E_F have predominantly $3d$ character, indicating that they are formed by the overlap of nonbonding d levels. In this, FeSi differs from the picture of a Kondo insulator in which a narrow f band (e.g., from Ce) hybridizes with a broad conduction band. For this reason we include FeSi in a broad class of "strongly correlated insulators."

We then calculated interband contributions to the imaginary part of the permittivity, $\epsilon''_{\mathrm{ib}}(\omega)$, in the limit of the electric dipole approximation, ignoring any relaxation effects,[12]

$$\epsilon''_{\mathrm{ib}}(\omega) = \frac{8\pi^2}{3\omega}\int \frac{d^3\mathbf{k}}{2\pi^3}\sum_{m,n}\frac{f(\varepsilon_{\mathbf{k}n})[1-f(\varepsilon_{\mathbf{k}m})]}{\varepsilon_{\mathbf{k}m}-\varepsilon_{\mathbf{k}n}} \times|\langle\psi_{\mathbf{k}m}|\mathbf{p}|\psi_{\mathbf{k}n}\rangle|^2\delta(\varepsilon_{\mathbf{k}m}-\varepsilon_{\mathbf{k}n}-\omega), \quad (1)$$

where $f(\omega)$ is the Fermi distribution function, $\varepsilon_{\mathbf{k}n}$ are the energy eigenvalues of momentum $\mathbf{k}$, and $\langle\psi_{\mathbf{k}m}|\mathbf{p}|\psi_{\mathbf{k}n}\rangle$ is the electric dipole matrix element. We discretized the $\mathbf{k}$ integration into a sum over nearly 3000 points (Fig. 3), verifying that finer meshes produced the same structures as coarser ones. However, checking the accuracy of the matrix elements, we found our calculation violates the sum rule, $\int \epsilon''_{\mathrm{ib}}(\omega)\omega\, d\omega = 2\pi^2 e^2 n_v/m$, over-

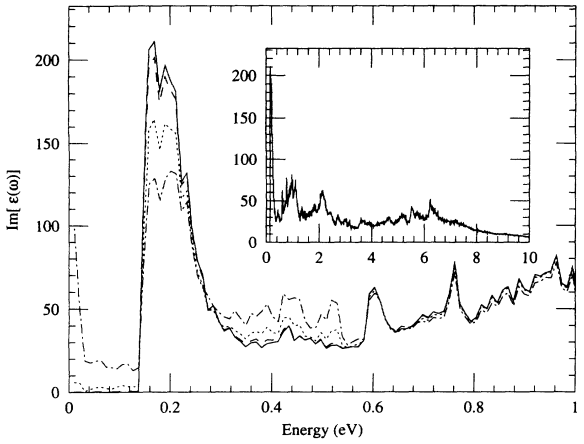

FIG. 3. ASW calculation of $\epsilon''(\omega,T)$ for FeSi. The solid, dashed, short dashed, and long-dashed–short-dashed lines represent $\epsilon''(\omega,T)$ for $T = 0$, 250, 500, and 1000 K, respectively.

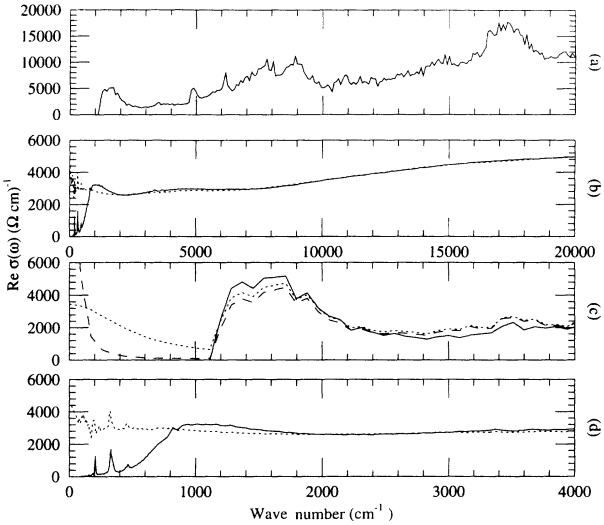

FIG. 4. Conductivity, $\sigma'(\omega,T)$ of FeSi. Part (a) is the ASW result at $T = 0$. Part (b) shows $\sigma'(\omega,T)$ from reflectivity measurements at 20 (solid) and 250 K (dotted) (Ref. 6). Part (c) illustrates $\sigma'(\omega,T)$ for the gap region, for $T = 0$ K (solid), and $T = 500$ K (dotted and dashed). The ASW calculation used T above the experimental value to reflect the larger optical gap. The dashed line is for $\tau = 2.0\times10^{-13}$ s which reflects the effect of electron-phonon scattering, and the dotted line is for $\tau = 10^{-14}$ s chosen to match experiment. Part (d) expands (b) near the gap.

counting the valence electron density n_v by about 30%. This degree of error is not unusual for electronic structure calculations.[18]

The oscillator strengths $(4/3)|\langle\psi_{\mathbf{k}m}|\mathbf{p}|\psi_{\mathbf{k}n}\rangle|^2/(\varepsilon_{\mathbf{k}m} - \varepsilon_{\mathbf{k}n})$ are quite small ($\approx 10^{-2} - 10^{-4}$) between the states near the gap due to selection rules. However, there are still peaks at 1600, 8000, and 17000 cm^{-1} stemming from transitions between the different $3d$ levels. A much broader and larger feature centered at 6 eV lies outside of the range of the experimental data of interest. The effect of temperature on interband transitions is fairly minor. Even for fairly high temperatures, there are only a few transitions within the gap at $T = 0$, and the main effect is a slight smearing in the spectrum.

However, this finite temperature smearing of the Fermi occupancies also creates valence holes and conduction electrons, which mediate the intrinsic conductivity. For the ac conductivity we can model these charge carriers with a Drude relaxation time τ. Since the conductivity should satisfy an overall sum rule, we can model the temperature-dependent conductivity $\sigma(\omega,T)$ as

$$\sigma(\omega,T) = \sigma_{\text{ib}}(\omega,T) + \frac{i\sigma(0,T)\tau}{(\omega + i\tau)}, \qquad (2)$$

where $\sigma_{\text{ib}}(\omega,T) = \omega\epsilon_{\text{ib}}(\omega,T)/(4\pi i)$, and we require $\int\sigma(\omega,T)d\omega$ to be constant.

For high-quality semiconductors at intermediate temperatures, τ is dominated by electron-phonon interactions. For an electron of energy ω, $\tau_{e\text{-}p} = (\hbar\rho c_s^2)/[\pi E_1^2 kTN(\omega)f(\omega)]$, where ρ is the mass density, c_s is the speed of sound, and E_1 is the linear energy shift of an electron from dilation of the lattice.[19] We estimate $E_1 \approx 1$ Ry by calculating the band structure for different lattice constants (neglecting the effect of shear) and averaging $E_1(\mathbf{k},j) = \delta\varepsilon_{\mathbf{k}j}/d$ where d is the dilation over several values of $\mathbf{k}$. We choose ω to maximize $[1-f(\omega)]N(\omega)$ below ε_f based upon our calculated DOS. Finally, taking $\rho c_s^2 = c_{11} = 330$ GPa from experimental data at 250 K (Ref. 20) this gives $\tau_{e\text{-}p} \approx 2\times10^{-13}$ s. The results of this approximation are shown in Fig. 4, along with recent infrared optical measurements.[6]

There are several notable features in this comparison. The most obvious is that the major structures are quite similar at low temperature, though the calculated $\sigma(\omega)$ is much larger than seen in experiment. This error could be the result of inaccuracies in the ASW calculation, since, as noted earlier, the overall sum rule is exceeded by 30% (however, experimental normalization problems cannot be ruled out). Secondly, even for fairly modest temperatures compared to the gap temperature $\Delta_g/2 = 850$ K, the spectral weight of the Drude peak is about half that required to fill the optical gap. This only partially accounts for the experimental observations, where the gap is filled. The lifetime of the intrinsic carriers from electron-phonon interactions is also much too long to match the data. Finally, the measured optical gap is found to be somewhat smaller than that predicted by band-structure calculations, in contrast to the usual case in semiconductors.

The "band-gap problem" in semiconductors stems from the interpretation of the electron eigenvalues as actual excitation energies. It is well known that this fails to properly account for contributions from exchange and correlation energies. For example, in Si, LDA underestimates the gap by about 0.6 eV.[21] In general, the error in the gap should reflect the on-site repulsion energy of the excited state, and thus be of the order $e^2/(\bar{\epsilon}\langle r\rangle)$, where $\bar{\epsilon}$ is the dielectric constant appropriate to the time scale of the excitation. From Kramers-Kronig transformation of both our calculation and infrared reflectivity data, $\epsilon'(0) > 150$, so the usual correlation energy errors in the band gap should be small.

Nevertheless, it is surprising to see the lowest peak at 1600 cm^{-1} for ASW, significantly above the experimental result of 1000 cm^{-1}. This would imply a shift of the band energies of about 40%. In the photoemission data this renormalization effect is not apparent for states where $|\omega - \varepsilon_f| > 0.8$ eV, and interpretation at lower energies is difficult. Given the differences between our calculation and LAPW ones,[15] this shift may be simply ascribed to errors in the ASW; however, this sort of renormalization reminds us of the mean field solutions for the Kondo lattice.[22] In that case the renormalized energies are exponential functions of the bare band parameters. Such a strongly correlated state would also likely drastically change the scattering rate of the intrinsic carriers.

A strongly increased scattering rate would partially explain the closing of the gap with increasing temperature. Looking at the ASW spectrum for T =500 K, we see that if we consider $\tau \approx 10^{-14}$ s the resulting broad Drude peak obscures the 0-K optical gap. Even so, however, a purely Drude origin for the low-frequency optical absorption would still show a strong gap edge near 0.1 eV which is not seen in optical measurements. This suggests that increased spin scattering at high temperatures is causing fairly major disordering of the coherent Bragg scattering assumed in the band-structure calculations, thus accelerating the disappearance of the gap and causing the system to behave more like a dirty metal than a thermally excited insulator. In fact, resistivity measurements deviate from activated behavior above about 200 K.[6]

We can also compare this scattering rate using dc conductivity measurements. Taking the carrier density from our calculation, $\sigma m^*/m = ne^2\tau/m = 3000\ \Omega^{-1}\,cm^{-1}$. Comparing this to measurements of FeSi, where $\sigma \approx 600\ \Omega^{-1}\,cm^{-1}$, at 250 K we find good agreement for $m^* = 5$ which is consistent with the band structure.

In summary, we have calculated various electronic properties of FeSi using an ASW method to determine what aspects of the charge excitation spectrum may be relevant to its unusual magnetic behavior. We find that one-electron theory predicts a set of narrow $3d$ bands near ε_f, which can potentially lead to strongly correlated behavior. Comparing the infrared reflectance spectra with the ASW spectra suggests some bands are renormalized towards ε_f. This renormalization would imply that the behavior of FeSi goes beyond the spin fluctuation picture of Moriya, and is evidence that strong electron correlations also alter the charge excitations in FeSi. The temperature dependence of the calculated optical response shows that while simple thermally activated carriers can partially account for the filling of the observed optical gap, strong scattering mechanisms are necessary, and the number of carriers generated is still somewhat low to account for the observations. Gaining a better understanding of the temperature-induced loss of coherence in FeSi will require further development in the tools of many-body theory.

We would like to thank Z. Fisk, Z. Schlesinger, H. T. Zhang, and J. Sarrao for bringing FeSi to our attention, as well as providing us with much data and many useful suggestions. We thank L. Mattheiss for sending us a prepublication copy of his LAPW calculation for FeSi and C. Sommers and V. L. Moruzzi for assisting us in using their ASW program. We would also like to thank W. Harrison for helpful discussions. This work was supported by the U.S. Department of Energy under Contract No. W7405-ENG-36.

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