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Results for β-$FeSi_2$ obtained from self-consistent calculations with the augmented spherical wave *ab initio* band-structure method are presented. In accordance with several experimental findings, β-$FeSi_2$ is found to be a semiconductor. The calculated gap is 0.44 eV and is indirect. The smallest direct gap is 0.46 eV and has a vanishingly small oscillator strength. The first across-gap transition with an appreciable oscillator strength has a corresponding energy gap of 0.77 eV.

Silicides form an important group of compounds for state-of-the-art semiconductor technology. Their bulk and thin-film properties are being investigated experimentally and theoretically.[1–5] The majority of the silicides turn out to be metallic.[1] There are clear indictions, however, that some silicides, e.g., $CrSi_2$ and β-$FeSi_2$ are semiconductors.[1–3] These could have interesting applications in future optoelectronic devices. It is therefore crucial to know whether these materials are indeed semiconductors and what the strengths of the optical transitions across the gap are. The purpose of the present work is to calculate the electronic properties of β-$FeSi_2$ using the augmented spherical wave (ASW) *ab initio* band-structure method.[6]

The calculations for β-$FeSi_2$ were performed using the crystallographic data from Ref. 7. The orthorhombic unit cell contains 48 atoms within a total of four inequivalent atomic sites, two for Fe and two for Si, indicated by Fe_I, Fe_{II}, Si_I, and Si_{II}, respectively. A self-consistent potential was generated by solving the Kohn-Sham equations[8] iteratively using the ASW basis set[6] within the local density approximation (LDA) for the exchange and correlation functional.[8] Scalar-relativistic effects were ignored. The ASW basis set consisted of 4*s*, 4*p*, and 3*d* orbitals centered at each Fe, and 3*s*, 3*p*, and 3*d* orbitals centered at each Si site.[9] All the atomic sphere radii were taken to be equal. Eight special *k*-points in the irreducible wedge of the Brillouin zone were used. The self-consistency process was stopped when the Hankel and Bessel energies of all atoms changed less than 0.1 mRy per iteration.

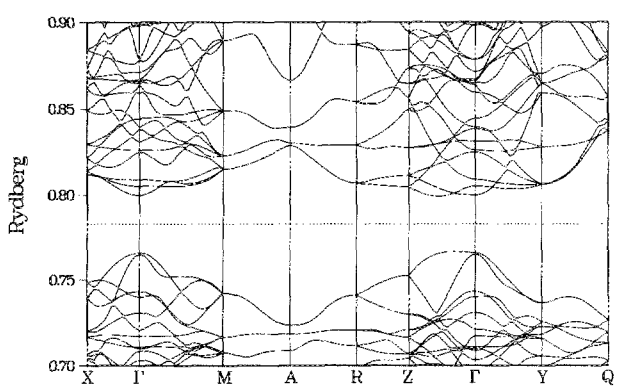

FIG. 1. Band structure of β-$FeSi_2$ near the gap.

The calculated results for the band-structure and density of states (DOS) of β-$FeSi_2$ are presented in Figs. 1 and 2. The dashed line represents the Fermi level. From these figures the most important conclusion of the present work can be drawn immediately: β-$FeSi_2$ is found to be a semiconductor. Moreover, from Fig. 1, β-$FeSi_2$ can be seen to have an indirect gap of 0.44 eV along Γ-*Z*. At Γ the direct gap is 0.46 eV. This value for the calculated gap depends on the ratio of the atomic sphere radii of Fe and Si, $r \equiv R_{Fe}/R_{Si} = 1$. For $r = 1.1$—roughly corresponding to the covalent radii of Fe and Si—and $r = 0.9$ we obtain a value of 0.47 and 0.40 eV for the direct gap, respectively. Within the valence or conducting band energy differences depend much less on this ratio; e.g., the energy difference between Γ and *Z* at the top of the valence band, $E_{\Gamma\text{-}Z}(n = 128)$, equals 0.212 and 0.203 eV for $r = 1.1$ and $r = 0.9$, respectively. All subsequent results are

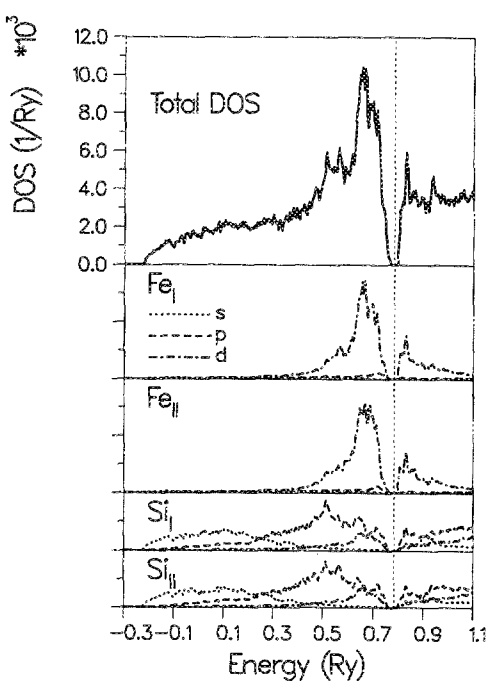

FIG. 2. Density of states (DOS) of β-$FeSi_2$ in units of number per states per unit cell per Rydberg. The number of *k*-points in the irreducible wedge of the Brillouin zone was 216 in this calculation. The subfigures contain the partial densities of states per atom per angular momentum number ($l = 0,1,2$: *s*, *p*, *d*). The dashed vertical line represents the Fermi level. All figures have the same vertical scale.

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for $r = 1$ (Ref. 10) and have been checked to have a similar dependence on the ratio r.

From Fig. 2 the global origin of all states can be traced. At low energies (below 0.2 Ry) the valence-band states contain mainly Si-s character. At higher energies (from 0.2 Ry on) the valence-band states contain more Si-p character. Near the gap (0.5–1.1 Ry) the valence-band states and the conduction-band states originate mainly from Fe-d states and are hybridized with Si-p and Si-d states. The important conclusion that can be drawn from this figure is that all states around the gap have mainly Fe-d character.

For the optical properties of β-$FeSi_2$ the states near the top of the valence band and the bottom of the conduction band are relevant. The across-gap oscillator strengths at Γ between these bands can be calculated directly using the ASW eigenfunctions[11] and are found to be extremely small ($<10^{-5}$). The dimensionless oscillator strength f_{mn} between two bands m and n with energies E_n and E_m, respectively, is defined as $f_{mn} = 4P^2_{mn}/(E_m - E_n)$, where P_{nm} is the expectation value of the impuls operator between the states m and n. These calculated oscillator strengths have been shown to be accurate on a level of 20% for a series of metals and III-V semiconductors.[11] A small value for the across-gap oscillator strength was to be expected since the states both above and below the gap consist mainly of Fe-d states with some Fe-p and Si-p states mixed in (see Table I). The first nonzero across-gap oscillator strength is between the conduction-band state $m = 129$ and the valence-band state $n = 126$ and equals 0.356 62 (cf., the calculated and experimental values for the across-gap oscillator strength of the direct semiconductor GaAs are 15.5 and 19.0, respectively[11]); the calculated energy difference between these states equals 0.77 eV. Similar numbers for the oscillator strengths are found for other $\mathbf{k}$ vectors in the Brillouin zone. For example, at Z the across-gap oscillator strength $f_{128\text{–}129}$ is less than 1×10^{-5}; halfway along Γ-Z it equals 0.01.

Would $FeSi_2$ also be semiconducting if it had a related but different crystal structure? To gain some insight into this question I have performed *ab initio* band-structure calculation of $FeSi_2$ in the related[7] C1 and C16 structures. In both cases a metal was found. Apparently, the distortion from the C1 (or C16) to the β structure is necessary if $FeSi_2$ it is to be semiconducting in these sorts of structures. Note that $CoSi_2$ has the C1 structure and is found to be a metal.[1]

I shall now compare the calculated results for β-$FeSi_2$ with the experimental findings. First, it should be noted that LDA-calculated gaps are usually too small as compared to the experimentally determined gaps (e.g., for silicon the ASW result for the indirect gap E_G is 0.50 eV). However, these results apply primarily to s-p gaps. It is conceivable that for β-$FeSi_2$ the calculated results are more accurate since an energy difference between very similar states, Fe-d states, is involved. Several interpretations of the calculated results are therefore possible. Bost and Mahan find a direct transition of 0.89 eV in their reflection and transmission measurements on β-$FeSi_2$ films and some weak transitions at energies down to 0.45 eV.[2] A conventional interpretation of the experimental results follows from assuming that the calculated gap is too small by 50% (in this case) and that all the experimentally observed transitions below 0.89 eV are due to defects.[2] The small (0.01) but nonzero oscillator strength at half-way along Γ-Z would allow for an almost direct transition at 0.88 eV (2×0.44) albeit a very weak one. Another possible interpretation based on the results of the calculation is the following: the measured direct transition at 0.89 eV corresponds to the first calculated nonzero direct across-gap transition and has a calculated corresponding energy gap of 0.77 eV. It is a Fe_I-d to Fe_{II}-d transition (see Table I) and thus this d-d gap is only off by 16%. The measured weak transitions from 0.45 eV on are weak (phonon-assisted) transitions. From the calculations these are expected to start from energies of 0.44 eV, the calculated indirect gap of β-$FeSi_2$, on. The second interpretation seems favorable since it is in general agreement with both the calculated band gaps and the calculated oscillator strengths.

In conclusion, from an *ab initio* band-structure calculation β-$FeSi_2$ is found to be a semiconductor with an indirect gap of 0.44 eV. The across-gap oscillators strengths for these transitions are found to be extremely small, whereas the first transition with an appreciable oscillator strength has a corresponding gap of 0.77 eV. The material β-$FeSi_2$ is therefore an unlikely candidate for light-emitting applications.

Note added: N. E. Christensen has obtained very similar results for β-$FeSi_2$ using the LMTO method except that the gap is 0.8 eV.[12]

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TABLE I. Approximate composition of the states around the gap at Γ. Fe_I, Fe_{II}, Si_I, and Si_{II} symbolize the inequivalent positions in the unit cell.[a]

State No.	p-Fe_I	d-Fe_I	p-Fe_{II}	d-Fe_{II}	p-Si_I	p-Si_{II}
$n = 126$	0.11	0.52	0.09	0.05	0.14	0.09
$n = 127$	0.11	0.09	0.03	0.53	0.21	0.05
$n = 128$	0.13	0.13	0.13	0.20	0.18	0.14
gap						
$m = 129$	0.01	0.21	0.00	0.64	0.02	0.01
$m = 130$	0.04	0.48	0.00	0.24	0.05	0.14
$m = 131$	0.01	0.44	0.00	0.45	0.01	0.02

[a] See Ref. 7.

[1] See, e.g., M. A. Nicolet and S. S. Lau in *VLSI Electronics: Microstructure and Science*, (Academic, New York, 1983), Vol. 6, pp. 330–464, and references therein.
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[9]Empty spheres were not included in the calculation. Although the structure contains some holes (see Ref. 7) the overlap between the different atomic spheres is only marginally improved by introducing empty spheres.

[10]An optimum value for atomic sphere ratio r would minimize the total energy. Unfortunately, the approximations basic to the ASW and alike methods usually prevent such a minimum to exist and, moreover, to be not unambiguously interpretable. The most important approximation (that the atomic spheres constitute the entire volume) makes the atomic spheres overlap each other. Different ratios r result in different parts of space to be included or excluded. Therefore, two calculations with different ratios r cannot be compared on the basis of the total energy. The minimum overlap between the atomic spheres in th β-$FeSi_2$ structure corresponds to $r \simeq 0.9$. Another approximation (that the potential is spherical within an atomic sphere) cannot be tested within the method itself. From data on atomic radii a value of $r \simeq 1.1$ would result. Therefore, $r = 1$ seems a reasonable choice.

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[12]N. E. Christensen (to be published).

Spectral properties of rf emission from high T_c films

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Spectral properties of rf radiation from intrinsic Josephson junctions in high T_c Y-Ba-Cu-O thin film have been measured in the frequency range up to 1.5 GHz. Narrow emission lines with the 3 dB bandwidth of the order of 20 MHz were detected indicating that Josephson clusters radiate coherently. Synchronization conditions are determined by dc current and external magnetic field bias. Frequency locking of radiation to external resonant circuit was also observed. Spectral line narrowing due to resonant lock was distinguished from the coherence-induced narrowing by different tuning properties of the emission line. Noncoherent Josephson radiation manifests itself as a broadband background noise increase. A pronounced $1/f$-like tail sensitive to dc bias and magnetic field was observed in a low frequency part of the spectrum.

Oxide superconductors usually grow in the form of a random collection of superconducting grains separated by nonsuperconducting material. Structure imperfections and grain boundaries locally depress superconductivity and act as Josephson type weak links between superconducting regions. Intrinsic Josephson junctions frequently dominate the superconducting properties of a high T_c (HTC) superconductor.[1–3] Although the nature and exact physical properties of the involved junctions are not known, one should always expect significant electromagnetic radiation due to ac Josephson effect whenever the intrinsic HTC junctions are biased by a dc voltage.

Pronounced electromagnetic emission from dc current biased Y-Ba-Cu-O (YBCO) thin films attributed to the radiating Josephson junctions have been recently observed by us in the microwave X-band.[4,5] Careful examination of the magnetic field dependence of the radiated rf power led us to believe that the emission originates from synchronously radiating intergranular Josephson clusters. However, we were unable to provide a direct experimental evidence for the synchronization of the radiating multijunction cluster. Such evidence can be obtained by the investigations of spectral properties of the emitted radiation. In fact, synchronization of several radiating oscillators should be reflected by relatively narrow lines in the frequency spectrum of the emitted energy. In this communication we report on our measurements on spectral properties of the radiation emitted from current biased HTC-YBCO granular thin films in the radio frequency band. Since the mechanism of emission in rf bands is the same as in the microwave bands, the experiment provides a direct evidence for the coherence in radiating intrinsic HTC Josephson cluster.

The linewidth of a classical radiating Josephson junction is determined by low-frequency voltage fluctuations that frequency modulate the radiated rf power according to Josephson voltage-frequency relation. The effective low-frequency noise voltage has two components. One is related to the original low-frequency fluctuations in the junction, while the second one is associated with the high-frequency noise down-converted to low frequencies in the mixing process with the fundamental harmonic of the Josephson oscillations. The down-converted noise consists of about 50% of the total low-frequency noise for the junction bias voltage close to zero and decreases considerably with increasing bias.[6] Assuming the low-frequency fluctuations in the Johnson–Nyquist form, the minimum linewidth of the Josephson emission in the resistively shunted junction (RSJ) approximation can be expressed as

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