PHYSICAL REVIEW B VOLUME 44, NUMBER 16 15 OCTOBER 1991-II

First-principles electronic structure and optical properties of $CrSi_2$

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(Received 20 May 1991)

Results for the electronic structure and optical properties of $CrSi_2$ as obtained from *ab initio* self-consistent augmented-spherical-wave calculations are presented. Further evidence of the semiconducting nature of pure $CrSi_2$ is provided. The calculated gap is 0.21 eV and is indirect. Calculated absorption coefficients are in qualitative agreement with experiment. Across-gap oscillator strengths are extremely weak.

Transition-metal silicides constitute a class of materials with important applications in Si-based device technology.[1] Several of them have been identified as semiconductors (e.g., $CrSi_2$, MnSi, $MnSi_2$, β-$FeSi_2$, $LaSi_2$, and $ReSi_2$), of which $CrSi_2$ has been reported to grow epitaxially on Si.[2,3] From an electrical characterization and analysis of optical-absorption data of thin films of stoichiometric $CrSi_2$, Bost and Mahan[4] conclude that $CrSi_2$ is an indirect semiconductor with a gap of 0.35 eV. As a result, it offers possibilities as a base material in heterojunction bipolar transistors and for optoelectronic devices operating in the infrared. Despite the potential technological importance of $CrSi_2$, few attempts have been made to calculate its electronic structure and optical properties.[5] In this work we present such a calculation with emphasis on the optical properties. The calculations are performed within the local-density approximation (LDA) to density-functional theory.[6] The one-particle equations are solved self-consistently by means of the augmented-spherical-wave (ASW) scheme.[7]

$CrSi_2$ possesses a hexagonal structure ($C40$) with space group $D_6^4-P6_222$ and lattice parameters $a=4.43$ Å and $c=6.36$ Å, and lattice matches Si(111) to 0.1%. The hexagonal unit cell contains 3 Cr and 6 Si atoms within a total of two inequivalent atomic sites, one for Cr and one for Si. Both the Cr and Si atoms are tenfold coordinated. The ASW basis set is taken to include 4*s*, 4*p*, and 3*d* orbitals on Cr, and 3*s*, 3*p*, and 3*d* orbitals on Si. The ratio of the atomic-sphere radii of Cr and Si, $r\equiv R_{\mathrm{Cr}}/R_{\mathrm{Si}}$, is chosen in accordance with the ratio of empirical atomic radii in crystals as compiled by Slater (i.e., $r=1.2$).[8] Scalar-relativistic effects are included. The Brillouin-zone sampling is performed at 40 special **k** points in the irreducible part.[9]

Calculations for several lattice parameters a (with c/a kept fixed at the experimental value) result in a bulk modulus of 1.06 Mbar and a minimum total energy for $a=4.46$ Å, which deviates from the experimental lattice parameter by less than 1%.

Results for the band structure and density of states (DOS) are presented in Figs. 1 and 2, respectively. In accordance with experimental findings, $CrSi_2$ is found to be an indirect-gap semiconductor. Figure 1 reveals an in-

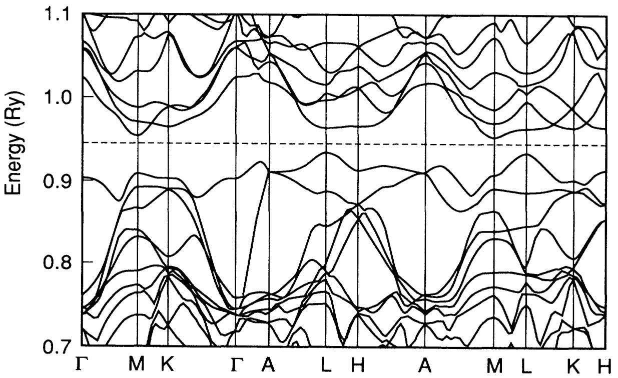

FIG. 1. Band structure of $CrSi_2$ along symmetry lines in the Brillouin zone of the hexagonal lattice.

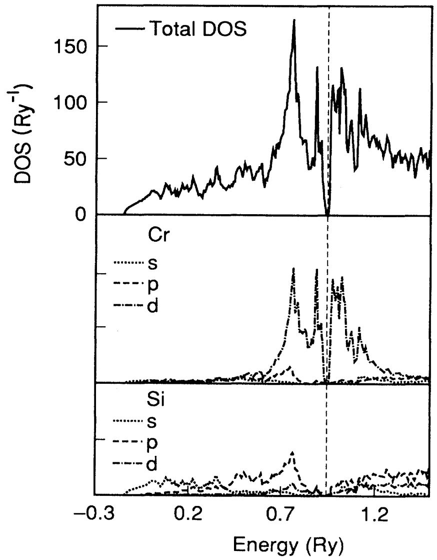

FIG. 2. DOS of $CrSi_2$ in units of the number of states per unit cell per Rydberg. The subfigures depict the partial density of states per atom for the angular momenta *s*, *p*, and *d*.

direct gap of 0.21 eV with a valence-band maximum at L and conduction-band minimum at M. At L the direct gap is 0.39 eV. For $r = 1.0$, we obtain values of 0.23 and 0.41 eV for the indirect gap and direct gap, respectively. This demonstrates that our results are not sensitive to the choice of atomic radii. Completeness of the basis set was tested by adding $4f$ orbitals to Cr, which resulted in values of 0.21 and 0.38 eV for the indirect gap and direct gap, respectively. Allowing for spin polarization did not result in any energy lowering. Adding spin-orbit coupling as a perturbation term to the Hamiltonian resulted in spin-orbit splittings always smaller than 10 meV. All subsequent results are for $r = 1.2$ and exclude $4f$ orbitals on Cr.

Our results for the band structure of $CrSi_2$ compare favorably with the outcome of recent linear augmented-plane-wave calculations of Mattheiss,[5] except for the fact that his calculations predict a gap of 0.30 eV which is somewhat larger than ours.

Tracing the global origin of all states from Fig. 2 leads us to conclude that the states around the gap have a predominantly Cr $3d$ character. Away from the gap, the valence-band and conduction-band states originate from Cr states hybridized with Si $3s$ and Si $3p$ states. Similar results were obtained for the semiconducting transition-metal silicide β-$FeSi_2$.[10]

For optoelectronic applications, the optical properties at frequencies close to the absorption edge are of principal interest. They are determined by the macroscopic dielectric function $\epsilon(\omega)$. From perturbation theory and the electric-dipole approximation (neglecting local-field effects), the imaginary part of the dielectric function is given by (in atomic units)[11]

$$\epsilon_2(\omega) = \frac{2\pi^2}{\omega} \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{m,n} f_{\mathbf{k}m}(1 - f_{\mathbf{k}n}) F_{mn}(\mathbf{k}) \times \delta(E_{\mathbf{k}n} - E_{\mathbf{k}m} - \omega) , \quad (1)$$

where

$$F_{mn}(\mathbf{k}) = \frac{1}{3} \frac{4|\mathbf{p}_{mn}(\mathbf{k})|^2}{E_{\mathbf{k}n} - E_{\mathbf{k}m}} \quad (2)$$

is the dimensionless oscillator strength for the absorption of "unpolarized" light between states m and n with energies E_m and E_n, respectively. The prefactor 2 in Eq. (1) accounts for spin degeneracy. The occupation number $f_{\mathbf{k}n}$ is the zero-temperature Fermi distribution function for state n and wave vector $\mathbf{k}$. $\mathbf{p}_{mn}$ in Eq. (2) is the expectation value of the momentum operator between states m and n. Oscillator strengths calculated with the ASW method have been shown to be accurate at the level of 20% for a series of metals and III-V semiconductors.[12] The across-gap oscillator strength at L is found to be very small (0.021). At M it amounts to 0.22 (for comparison, the calculated across-gap strength of the direct-gap semiconductor GaAs equals 15.5). Similar values are found at other $\mathbf{k}$ vectors. These small values are to be expected since the states just above and below the gap have mainly Cr $3d$ character (cf. Fig. 2). Although the momentum matrix elements $\mathbf{p}_{mn}$ become appreciable for states m and n lying further apart, the oscillator strengths remain rather small (they nowhere exceed 1.0). Results for the dielectric function are depicted in Fig. 3. The reciprocal space integration was performed by histogram sampling in energy intervals of 50 meV using 1651 special $\mathbf{k}$ points in the irreducible part of the Brillouin zone.[9] All states in the valence band of width 15 eV and in the conduction band up to 29 eV were included in the summation. The completeness of the basis set was tested with respect to the asymptotic behavior of ϵ_2 at high energies. The real part of the dielectric function, $\epsilon_1(\omega)$, was calculated from the Kramers-Kronig transformation of $\epsilon_2(\omega)$. Similar calculations performed by us for Si resulted in $\epsilon_1(0) = 12.2$ and a plasmon peak in the electron-energy-loss function $\mathrm{Im}[-1/\epsilon(\omega)]$ at 15.9 eV (these results are in good agreement with the experimental values of 11.9 and 16.4 eV, respectively). The fine structure in Fig. 3 is not due to noise caused by poor sampling statistics, since it remains unaltered upon increasing the energy interval width and decreasing the number of sample points.

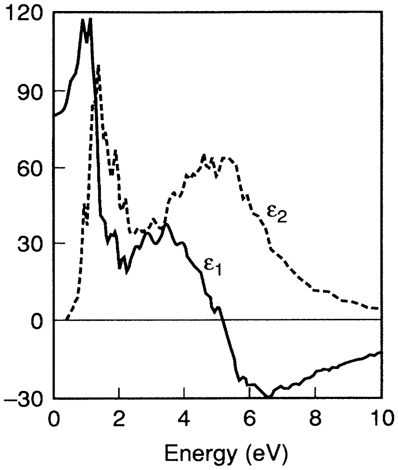

FIG. 3. The real (ϵ_1, solid line) and imaginary (ϵ_2, dashed line) part of the calculated dielectric function.

From the band structure and $\epsilon_2(\omega)$ as depicted in Figs. 1 and 3, respectively, we infer that optical absorption for energies not exceeding 0.8 eV is due solely to interband transitions between the highest valence-band state and the lowest conduction-band state. Beyond 0.8 eV, transitions between states lying further apart come into play, leading to absorption maxima at 1.3 and 5.6 eV.

We proceed with a comparison of our results with the experimental findings of Bost and Mahan.[4] For that purpose we calculated the absorption coefficient $K(\omega)$ from

$$K(\omega) = \frac{2\omega}{c} \mathrm{Im}[\epsilon(\omega)^{1/2}] \quad (3)$$

and display its square root together with the experimental results in Fig. 4. The existence of an indirect gap should show up in the experimental spectrum as a region with linear dependence on $K^{1/2}$. This linear region is present between 0.5 and 0.7 eV and has an intercept near 0.35 eV, which leads Bost and Mahan to conclude that

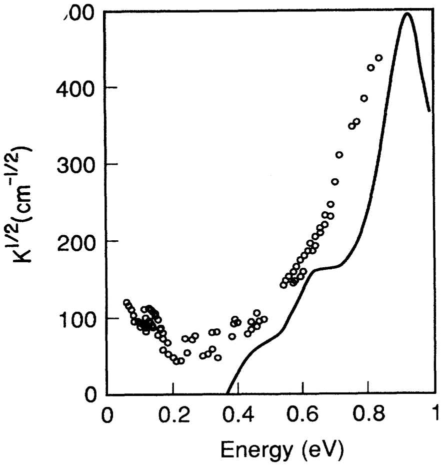

FIG. 4. Calculated (solid line) and measured (open circles, Ref. 4) results for the square root of the absorption coefficient K near the absorption edge.

$CrSi_2$ is a semiconductor with an indirect gap of 0.35 eV. The experimental absorption coefficient being nonzero for energies below 0.35 eV is ascribed to scattering due to the polycrystalline nature of their samples. Furthermore, stoichiometric $CrSi_2$ is reported to be a p-type degenerate semiconductor (hole concentrations $\simeq 8 \times 10^{20}/cm^3$ at room temperature), which suggests that intraband absorption could also play a role at low energies.[1] Although in qualitative agreement, the calculated absorption coefficients as displayed in Fig. 4 are generally too low as compared to the experimental results. Finally, it should be noted that LDA gaps are usually underestimated: whereas Bost and Mahan infer from their data an indirect gap of 0.35 eV, our calculated value corresponds to 0.21 eV. Equally, they suggest a direct transition at 0.67 eV as compared to a calculated value of 0.39 eV.

In conclusion, first-principles calculations of the electronic and optical properties of $CrSi_2$ provide further evidence that $CrSi_2$ is a semiconductor with an indirect gap. Calculated and measured absorption coefficients are in qualitative agreement. Since the calculations show only weak across-gap transitions, the use of pure $CrSi_2$ as a material for light-emitting applications seems unlikely.

We are grateful to D. Oostra for bringing the subject to our attention and we acknowledge the stimulating support of M. F. H. Schuurmans.

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