Quasiparticle band structure of HgSe

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Motivated by a recent discussion about the existence of a fundamental gap in HgSe [Phys. Rev. Lett. **78**, 3165 (1997)], we calculate the quasiparticle band structure of HgSe within the *GW* approximation for the electron self-energy. The band-structure results show that HgSe is a semimetal, which is in agreement with most experimental data. We observe a strong wave-vector dependence of the self-energy of the lowest conduction band, leading to an increased dispersion and a small effective mass. This may help to interpret recent photoemission spectroscopy measurements. [S0163-1829(98)50816-8]

The II-VI compound HgSe has recently attracted interest for a unusual reason: it is unclear if the material is a semiconductor or a semimetal.[1] Most experiments, such as magnetoabsorption measurements[2,3] or optical experiments[4,5] indicate that HgSe has an inverted band structure with a fundamental gap which is exactly zero, i.e., it is a semimetal (for a comprehensive compilation of experimental results see Ref. 4). Recent angle-resolved photoemission spectroscopy (ARPES) experiments by Gawlik *et al.*,[1] which were carried out for *n*-type HgSe with the Fermi level above the valence-band maximum (VBM), on the other hand, show only very weak photoemission between the VBM and some states at the Fermi level. From their data, the authors conclude that HgSe is not a semimetal but a semiconductor.

In this work, we address the contradiction between different experiments by means of calculating the quasiparticle band structure of HgSe and trying to interpret the experimental results accordingly. Only few calculations of the band structure of HgSe have been presented so far, all of them using empirical or semi-empirical methods.[6,7] Since they are based on experimental input data, they in principle cannot resolve the question of the existence of a gap in the band structure of HgSe. Here we present, to our knowledge, the first *ab initio* quasiparticle (QP) band-structure calculations for this material. In particular, we discuss the self-energy corrections of states near the valence-band maximum. Different from typical results for semiconductors, the corrections strongly depend on the wave vector. This influences the dispersion of the bands, as well as, their effective masses and their density of states.

We employ the *GW* approximation (GWA) (Refs. 8 and 9) for the electron self-energy to calculate the QP band structure. This method has been shown to yield very reliable band structures in excellent agreement with experiment for a large class of materials, including metals, semiconductors, and the semimetal α-Sn.[10–15] Gap energies are usually given within an uncertainty in the order of 0.1 eV. A *GW* calculation for HgSe should therefore allow one to resolve the question whether the fundamental gap of HgSe is nonzero or zero, i.e., whether HgSe is a semiconductor or a semimetal.

For determining the QP band structure of HgSe, we employ a procedure that has become state-of-the-art in band-

structure calculations.[10] We start with a density-functional theory (DFT) calculation within the local-density approximation (LDA), using norm-conserving pseudopotentials that are constructed following the prescription of Hamann.[16] We employ a Se^{6+} pseudopotential, as well as, a Hg^{20+} pseudopotential which treats all Hg semicore states ($5s$, $5p$, and $5d$) as valence states.[17] Spin-orbit interaction is included in the calculation by employing additional pseudopotentials.[18,19] From this calculation, we obtain LDA wave functions and energies. The LDA band structure is displayed in Fig. 1 as dashed lines. Based on these results, we construct the electron self-energy operator within GWA (for details, see Refs. 10, 14, and 20). We employ basis sets of localized Gaussian orbitals for the representation of the wave functions and all two-point functions. This allows for a very efficient description of the strongly localized Hg semicore states. The difference between the *GW* self-energy operator and the LDA exchange-correlation potential constitutes QP corrections to the LDA band structure, thus finally leading to the QP band structure of HgSe as shown in Fig. 1 (solid lines).

Both the LDA and the final *GW* QP band structure are semimetallic. The *s*-like Γ_6 state, which is above the VBM
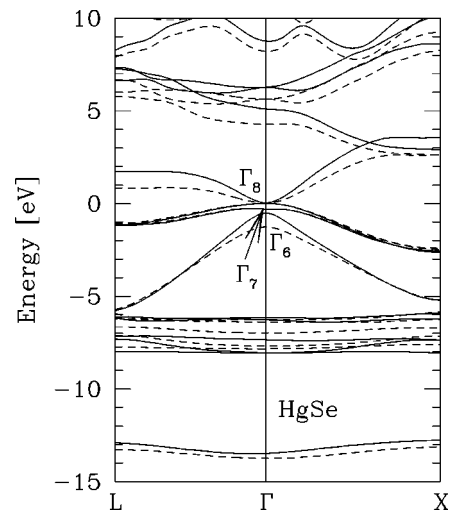

FIG. 1. Band structure of HgSe, as calculated within GWA (solid lines) and LDA (dashed lines), respectively.

in all II-VI semiconductors containing Zn or Cd,[21] has a much lower energy in HgSe due to the more attractive potential of Hg as compared to Zn or Cd. It is thus found below the VBM which is given by the Γ_8 state. This leads to the ''inverted band structure'' of the material. It is interesting to note that, near the Γ point, the respective bands do not simply cross, as one might expect from the inverted order of Γ_6 and Γ_8. Instead, the coupling between the states of the two bands leads to the formation of two new states. The respective two new bands repel each other and no crossing occurs even along high-symmetry directions.

The QP corrections of the lowest conduction band Γ_{8c} and the valence band Γ_{6v} are of particular interest. Near the Brillouin zone boundaries, the lowest conduction state (connecting to Γ_{8c}) is mostly formed by s orbitals, as is common in most II-VI semiconductors containing Zn or Cd. The QP band observes a nearly rigid energy shift of 0.8 eV at most wave vectors with respect to the p-like VBM. Such a shift is typical for conduction bands in semiconductors. The lowest one of the upper valence bands (connecting to Γ_{6v}), on the other hand, is formed by p orbitals, just as the highest valence states, for most wave vectors. Therefore, it does not observe a significant QP correction with respect to the VBM. Near the Γ point, however, this behavior changes drastically. Due to the inversion of the band structure, the lowest one of the upper valence bands couples to the lowest conduction band and changes gradually from a p state to an s state. At the Γ point, it has the Γ_6 symmetry which is usually found for the lowest conduction band in II-VI semiconductors. The state now observes a strong positive QP correction typical for the Γ_{6c} conduction band minimum of a semiconductor. Concomitantly the lowest conduction state Γ_{8c} is formed by p orbitals, just like Γ_{8v} and Γ_{7v}, instead of s orbitals. It has the same symmetry as Γ_{8v} and the two states are energetically degenerate both within LDA and GWA. Therefore, the QP correction of the state with respect to Γ_{8v} is zero. Resulting from these changes of the orbital composition of the states near the Γ point, a strong wave-vector dependence of the QP corrections is observed for the bands, and their dispersion is drastically increased. This clearly demonstrates that it is not necessarily the occupancy of a state which determines the size and sign of its QP corrections, but rather its wave function and symmetry.

The energy of Γ_6, i.e., the gap E_0 of the band structure, amounts to -1.27 eV in LDA. The state observes a positive QP correction of $+0.76$ eV. The resulting QP energy of Γ_6 amounts to $E_0 = -0.51$ eV. We thus find the Γ_6 state below the two states Γ_7 and Γ_8 that are split by $\Delta_0 = 0.30$ eV due to spin-orbit interaction. This is in contrast to the common assumption that Γ_6 should be *between* Γ_7 and Γ_8, i.e., $E(\Gamma_7) < E(\Gamma_6) < E(\Gamma_8)$ and $\Delta_0 > |E_0|$.[4] Based on this assumption on the ordering of the states, most experiments (such as, e.g., Shubnikov–de Haas measurements and infrared spectroscopy) report values of -0.3 eV to -0.2 eV for E_0 (see the compilation in Ref. 4). Our result of $E_0 = -0.51$ eV is somewhat lower than these data. However, the experimental results for E_0 might actually correspond to the position of the Γ_7 state instead of Γ_6. Our result of -0.30 eV for Γ_7 would then be in very good agreement with experiment. In Table I we compare the energies of several transitions between valence and conduction bands with avail-

TABLE I. Calculated band-structure transition energies for HgSe (in eV).

	This work	Experiment
$\Gamma_{8v} \rightarrow \Gamma_{7c}$	5.4	5.2[a]
$L_{3v} \rightarrow L_{1c}$	2.9	2.9[b]
$L_{3v} \rightarrow L_{3c}$	8.7	8.45[c]
$X_{5v} \rightarrow X_{3c}$	5.8	5.85[c]
$X_{5v} \rightarrow X_{1c}$	6.2	6.6[c]

[a]Reference 22.
[b]Reference 4.
[c]Reference 23.

able experimental data. We find very good agreement for all transitions.

Our QP band-structure results, as well as the results of most previous experiments, seem to be in contrast to the recent ARPES measurements on HgSe by Gawlik *et al.*[1] that showed very low photoemission (PE) intensity between the VBM and the Fermi level. From their data the authors conclude that HgSe is a semiconductor with a gap of $E_0 = +0.42$ eV between the occupied Γ_8 and the unoccupied Γ_6 state. We believe that the difference of 0.93 eV between our calculated E_0 (-0.51 eV) and this experimental result is way too large to be attributable to uncertainties in the measurement or in our calculation. Instead, we believe that the low PE intensity above the VBM might be due to the strong dispersion of the lowest conduction band near the Γ point. To discuss this, we calculate the density of states and compare it with the experimental PE spectra. We neglect the influence of transition probabilities, final states, and surface effects on the PE process. Therefore, only a semiquantitative comparison with experiment is possible. The essential aspect, i.e., the very low PE intensity above 0 eV, can, however, be discussed within these approximations.

The lowest conduction band has a much stronger dispersion than the two highest valence bands. The effective mass of the conduction band at the Γ point amounts to $m^* \approx 0.2$ within LDA which is much smaller than that of the valence-band maximum ($m^* \approx 1.1$). With the QP corrections, the dispersion of the conduction band is further increased (see the discussion above), and its effective mass is reduced to $m^* \approx 0.1$. In experiment, an even smaller mass between 0.03 and 0.06 is observed.[24] The effective mass of the VBM remains nearly unchanged; it amounts to 1.0 in the QP band structure compared to the experimental value of 0.78.[25] Due to its strong dispersion, the density of states (DOS) of the conduction band is much smaller than that of the highest valence bands. In Fig. 2 we display the calculated DOS corresponding to the QP band structure of Fig. 1. In the energy range between 0 eV end 1 eV, the DOS is two orders of magnitude smaller than the DOS of the highest valence states between -3 and -1 eV.

The ARPES measurements by Gawlik *et al.* were carried out with emission of electrons normal to the HgSe(100) surface, i.e., the wave vectors of the electrons are restricted to $\mathbf{k} = (k_x, 0, 0)$. Therefore, the total DOS as presented in Fig. 2 does not allow for a reasonable comparison with the measured spectra. Instead, the partial DOS corresponding to the Δ line of the band structure, i.e., $\mathbf{k} = (k_x, 0, 0)$ should be dis-
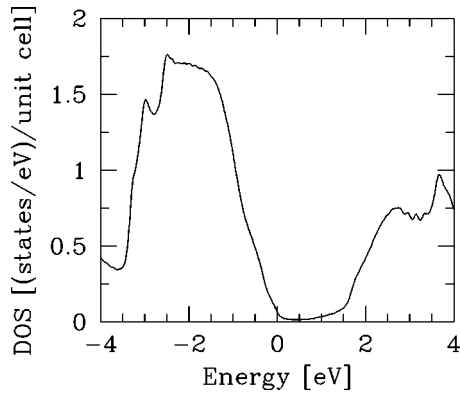
FIG. 2. Calculated total density-of-states of HgSe, corresponding to the QP band structure as presented in Fig. 1.

FIG. 3. (a) Calculated partial density-of-states (arbitrary units) along the Δ line [i.e., $\mathbf{k}=(k_x,0,0)$], as well as experimental ARPES spectra [(b), (c)] of the HgSe(001) surface by Gawlik *et al.*[1] The spectra were taken at normal emission with photon energies of 11 and 12 eV, respectively.

cussed. This Δ-line partial DOS is displayed in the upper panel of Fig. 3. Again, the DOS originating from the lowest conduction band is much smaller than the DOS due to the highest valence bands. The difference is less dramatic than in the total DOS due to the restriction of the wave vector to the one-dimensional Δ high-symmetry line.

We include in Fig. 3 two ARPES spectra from Ref. 1, taken at photon energies of 11 and 12 eV. The measurements were carried out at n-type HgSe with a Fermi level of $E_F=0.65$ eV. The spectra show PE from states up to 0.2 eV, as well as, between 0.4 eV and E_F. The latter was interpreted in Ref. 1 as a superposition of PE from the partially filled conduction band and a surface state at 0.5 eV. Between 0.2 and 0.4 eV, on the other hand, a very low PE intensity was observed. The authors interpreted this as a fundamental gap in the bulk band structure of HgSe which would thus be a semiconductor.

Based on our calculated Δ-line partial DOS, however, we believe that the measured PE spectra are not contradictory to a semimetallic band structure for HgSe. The Δ-line partial DOS is very low for energies above 0.2 eV. Since the measured effective mass for the lowest conduction band is even smaller than our theoretical result (see above), the DOS above the VBM can be expected to be even lower than indicated in Fig. 3(a). Hence, a very weak PE intensity has to be expected above 0.2 eV—as is, indeed, observed in experiment. Consequently, only a small portion of the observed PE intensity between 0.4 eV and E_F would be related to the bulk conduction band. Instead, the largest part of this PE feature would have to originate from a surface state or from intrinsic defect levels.
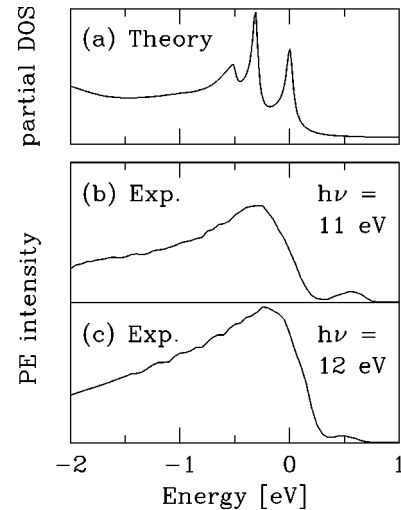
In conclusion, we have calculated the quasiparticle band structure of HgSe within the GW approximation. The theory results in a semimetallic band structure with an inverted fundamental gap of -0.51 eV. This finding is in agreement with most experimental data which indicate that HgSe is a semimetal. Resulting from the semimetallic band structure and the orbital character of the states, the quasiparticle corrections observe a strong wave-vector dependence. As a consequence, the dispersion of the lowest conduction band is drastically increased and its effective mass is strongly reduced, leading to a very small density-of-states of this band. This might be responsible for the very low PE intensity between the VBM and the Fermi level observed in the recent ARPES study.

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