

## Local-density theory of mixed-valence TmSe and the valence transition in Tm chalcogenides

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The first precise *ab initio* total-energy local-density calculation of the electronic structure of a mixed-valence compound, TmSe, correctly reproduces the observed lattice constant and a nonintegral  $f$  number for the ground state. The mixed-valence-to-integral-valence transition in the chalcogenides is shown to be connected to the opening of a gap between the  $f$  band and the conduction  $d$  band. Experimental volume-pressure relations cannot be explained without taking into account the interaction with the valence  $p$  band.

Mixed-valence materials display a wide variety of interesting physical phenomena<sup>1,2</sup> that arise from the interplay of localized  $4f$  electrons and itinerant conduction-band electrons. Most theoretical investigations of  $4f$ -related excited-state properties as observed in photoemission experiments are based on many-body model Hamiltonians<sup>3</sup> which include experimental values of the ground-state parameters. An *ab initio* total-energy theoretical description of the electronic structure of the ground state within density-functional theory has been nonexistent because (i) the applicability of local-density theory to the mixed-valence problem has been thought questionable and (ii) the presence of localized  $4f$  electrons requires extremely precise band-structure calculations in order to obtain reliable, converged results. We report here the first precise *ab initio* total-energy local-density calculation for a mixed-valence compound. An analysis of the results is consistent with the observation that the mixed-valence-to-integral-valence transition in the chalcogenides is connected to the opening of a gap between the  $f$  band and the conduction  $d$  band. We give evidence that the experimental volume-pressure relations cannot be explained without taking into account the interaction of the valence  $p$  band with the  $f$  band. Minimizing the total energy of TmSe as a function of volume correctly reproduces the experimental value of the lattice constant and yields a nonintegral  $f$  number for the ground state, also in agreement with experiment.

The total energy and the charge density of the interacting electrons are obtained by solving the well-known semi-relativistic<sup>4</sup> effective single-particle equations in the Hohenberg-Kohn-Sham<sup>5</sup> formalism. The exchange and correlation energy is approximated by the local form of Hedin and Lundqvist.<sup>6</sup> In our full-potential linearized augmented-plane-wave<sup>7</sup> (FLAPW) method all numerical errors are controlled and they can be made arbitrarily small. Numerical convergence tests for TmSe show a remaining relative error in the total energy of 0.3 mRy. The most important parameter in our calculations for TmSe is the number of APW's needed to describe the electronic structure. We use approximately 500 basis functions in order to accurately describe the  $4f$  electrons; a smaller number would lead to large errors in the total energy and in the relative positions of the eigenvalues of the  $f$  band. Without the

large Fourier components the  $4f$  electrons are spatially not sufficiently localized and the direct  $f$ - $f$  overlap becomes too large; this broadens the  $f$  band and shifts the minimum of the total-energy curve. Such a result clearly demonstrates the necessity of very precise band-structure calculations to evaluate the electronic structure of TmSe and related compounds.

The eigenvalue spectrum of the effective single-particle equations is a useful tool to study the mixed-valence-to-integral-valence transition in TmSe under (negative) pressure. While realistic quasiparticle excitation energies are obtained by solving the full Dyson equation, the eigenvalues of the Kohn-Sham equations, however, are certainly first-order approximations to these excitation energies, and an analysis of the eigenvalue spectrum has a qualitative meaning. As seen from Fig. 1(a), there is a distinct energy separation between the Se- $p$  and Tm- $f$  and  $-d$  bands except for the overlap shown on an expanded scale in Fig. 1(b). A study of the partial charge distributions shows that the size of the  $4f$  orbitals is almost volume independent and that they have a small density in the interstitial region. The radial extent of the valence  $p$  orbitals, on the other hand, scales with the lattice parameter. These orbitals also have a large density in the interstitial region and hence they (i) determine the actual lattice structure and (ii) must be an intermediate in transferring information concerning the  $f$  electrons to structural properties.<sup>8,9</sup>

A strong decrease with volume  $V$  is observed in both the  $f$ -band width and the size of the  $f$ - $d$  overlap. The  $f$ -band width is determined by the interaction with the conduction band (a standard Friedel resonance) and also by the interaction with the valence band, which pushes energy levels like  $\Gamma_{15}$  to higher values. The  $X_3$  level, the bottom of the  $d$  band, crosses the  $f$  band only in the vicinity of the  $X$  point. At  $V$  corresponding to a lattice constant of 6.17 Å, we find no  $f$ - $d$  overlap and a  $f$  band width of only 7 mRy or 0.1 eV (which still is larger than typical values extracted from experiments,<sup>10</sup> indicating the importance of self-energy corrections, multiplet structure, etc.). At this value of  $V$ , the valence of the Tm ions is +2, by necessity. We thus confirm the picture<sup>11,12</sup> that the integral-valence-to-mixed-valence transition in Tm chalcogenides is caused by the closing of a gap between the  $f$  band and the conduction

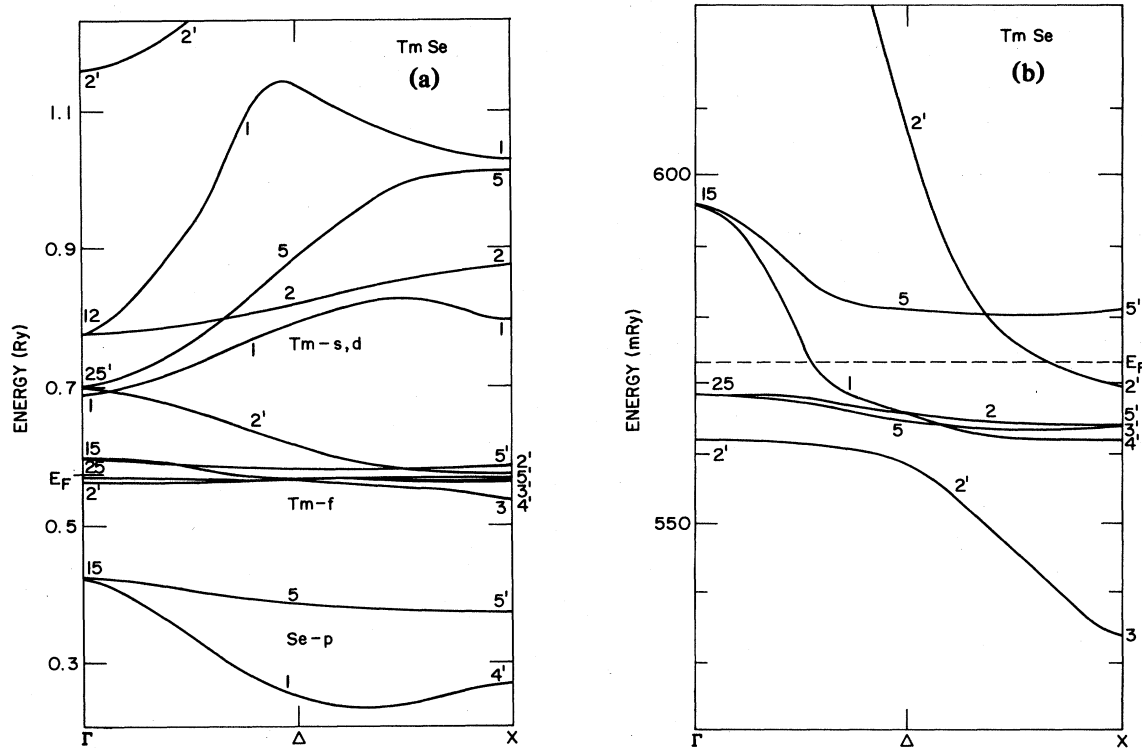


FIG. 1. (a) Energy spectrum of the Kohn-Sham equations for TmSe at the equilibrium lattice constant showing the relative positions of the different bands. (b) A blowup of the region near  $E_F$ .

band. We do not provide numerical values of the valence because there is no straightforward way to evaluate the  $f$  contribution in the interstitial region. One can make a comparison with experiment by calculating the matrix elements involved in a given experiment.

The transition from integral-valence-to-mixed-valence behavior can be studied in a continuous way as a function of pressure in the ternary alloy system  $\text{TmSe}_{1-x}\text{Te}_x$ .<sup>13</sup> In this case there appears to be a contradiction between values of the valence as derived from the experimental values of  $V$  and magnetic moment. Changes of  $V$  as a function of pressure indicate a continuous change in  $4f$  occupation number, with a maximal effect at a pressure where the bulk modulus is very small.<sup>13,14</sup> On the other hand, the value of the magnetic moment is constant up to this pressure<sup>13</sup> and starts to deviate from the value for integral-valence Tm only above this pressure. This paradox is immediately resolved when we take into account the interactions with the valence  $p$  band. Group theory indicates that at the high symmetry points  $\Gamma$  and  $X$  there is no hybridization between the  $f$  and the  $d$  band. At  $\Gamma$ , only the  $\Gamma_{15}$  level interacts with the  $p$  band. The band structure near  $\Gamma$  in Fig. 1(b) shows that the  $p$ - $f$  hybridization is important: The position of the  $\Gamma_{15}$  level is much higher than one would extrapolate from the flat  $f$  bands in other parts of the Brillouin zone.

Decreasing  $V$  increases the width of the Tm  $s$ - $d$  band and the  $X_3$  level comes down in energy and narrows the gap between the  $d$  and  $f$  band. Near the  $X$  point the  $f$  and  $d$  bands do interact and this interaction becomes stronger when the energy differences get smaller (which follows immediately from perturbation theory). Translated into an or-

bitual picture, the result of the  $X_3$  level coming down in energy is an increased hybridization of  $4f$  orbitals with  $5d$  orbitals on the neighboring Tm atoms; that leaves the local moments unaffected but changes the hybridization with the  $p$  band and hence affects the lattice properties. When the  $X_3$  level crosses the  $f$  band, the  $4f$  orbitals on a given atom are depopulated and hence the moment also changes. When the  $X_3$  level is well below the  $f$  band the region in reciprocal space in which the  $f$ - $d$  hybridization takes place is large and the anticrossings separate  $d$ - and  $f$ -like bands far apart. On the other hand, when the  $X_3$  level is in the middle of the  $f$  band,  $d$ - and  $f$ -like levels are forced to be in the same small energy range near the  $X$  point and this has strong effects on the total energy (as seen in a softening of the bulk modulus). Hence, a determination of the valence by experiments which involve the  $f$  orbitals directly, such as susceptibility,<sup>13</sup> photoemission,<sup>15</sup> or x-ray absorption<sup>16</sup> measurements, yields an accurate estimate of the amount of overlap of the Tm  $d$  and  $f$  bands. Structural properties, on the other hand, are derived from the Se- $p$  valence band and mainly reflect changes in the tails of the  $f$  orbitals; here, we find an amplification of changes in the hybridization of the  $f$  band which already occur before there is an actual  $f$ - $d$  overlap. As a result, any *ab initio* description of pressure-induced changes of the valence has to include this Se- $p$  band.

Quantitative predictions concerning the actual ground state of TmSe can be made by studying the total energy  $E_{\text{tot}}$  as a function of  $V$ , a dependence which is one of the basic and physically meaningful relations within density-functional theory. Our results are given in Fig. 2. The solid line indicates a quadratic fit to the calculated points and this parabola

la is used to determine the values of the equilibrium volume and bulk modulus  $B$ . As can be seen in Fig. 2, the use of a parabola to describe our data is consistent with the relative errors in  $E_{\text{tot}}$ . The experimental<sup>13,17</sup> ( $5.69 \pm 0.02 \text{ \AA}$ ) and theoretical ( $5.683 \pm 0.005 \text{ \AA}$ ) values for the lattice constant agree extremely well, indicating that all theoretical errors in the description of the  $4f$  electrons are systematic and are independent of  $V$  near the equilibrium configuration. At this value of the lattice constant we find an overlap between the  $f$  and  $d$  bands, and hence we find the ground state of TmSe to be mixed valent. On the other hand, the theoretical value for  $B$  ( $68 \pm 10 \text{ GPa}$ ) is larger by almost a factor of 2 than experiment<sup>13</sup> ( $35 \pm 10 \text{ GPa}$ ) although the error bars are large too. Note, however, that the value of the bulk modulus is strongly pressure dependent: a 1.3% decrease of the lattice constant is sufficient to make  $B = 70 \text{ GPa}$ .<sup>18</sup> We have to keep in mind that the TmSe samples used in the experiments contain up to 3% of Schottky defects.<sup>17</sup> As a result,  $B$  is possibly smaller than that of pure TmSe, because the presence of vacancies will make the lattice softer. The effect of vacancies and stoichiometry<sup>17</sup> on the lattice constant is much smaller and will not change the good agreement between theory and experiment.

In our description of the  $f$  electrons we have made three approximations which do not affect the relative values of  $E_{\text{tot}}$  in a severe manner. First, spin-orbit coupling is neglected. The effect on the  $E_{\text{tot}}$  scales with the inverse second power of the fine-structure constant and is small for an almost filled band. The resulting error is mainly systematic and does not affect the structural properties. We have determined the relative changes in  $E_{\text{tot}}$  and find that this interaction changes our value of the lattice constant by less than 1%. The second approximation is the neglect of long-range magnetic order. This is also a small effect, as reflected in the extremely low value of the Néel temperature<sup>19</sup> ( $3 \text{ K}$  or  $0.2 \text{ mRy}$ ). Most experiments are performed at higher temperatures and show that long-range magnetic order does not affect the main characteristics of the mixed-valence ground state. Also note that density-functional theory does not exclude the existence of local moments although, at present, there is no good way to evaluate the characteristics of these moments within the theory. Finally, the use of the local-density approximation for the localized  $4f$  electrons results in large absolute errors. Our results, however, reproduce the experimentally observed lattice constant and hence all errors due to the  $4f$  electrons must be systematic. Results for systems where direct  $f$ - $f$  overlap is important for the chemical bond show discrepancies in the lattice constant to be larger than a few percent. Hence, in TmSe the direct  $f$ - $f$  overlap is not an important contribution to the ground-state energy.

The effect of these approximations on the eigenvalue spectrum is larger, but does not affect our qualitative pic-

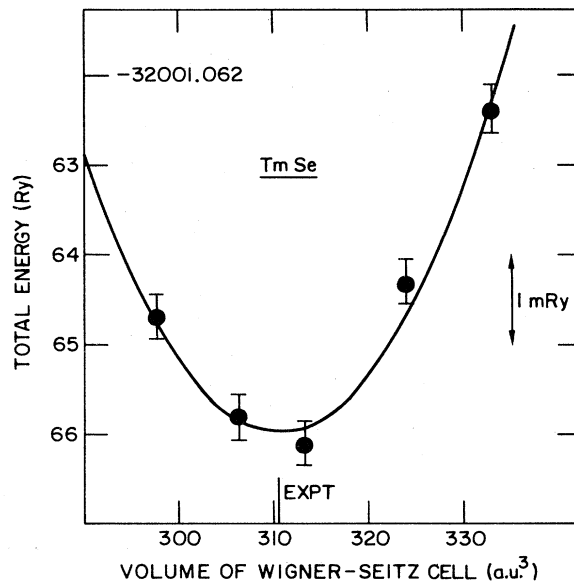


FIG. 2. Total energy of TmSe as a function of volume. The solid line is a parabolic fit to our data points.

ture of the valence transition. A study of the  $\text{TmSe}_{1-x}\text{Te}_x$  system<sup>13</sup> shows that we expect a transition to integral-valence  $\text{Tm}^{2+}$  at a lattice constant of  $6.0 \text{ \AA}$ , which is 3% smaller than the value we have found. This indicates that for a quantitative description of the valence transition one certainly has to consider spin-orbit coupling and magnetic ordering and possibly effects beyond the local-density approximation.

We have shown that local-density-functional theory yields an accurate value of the lattice constant of mixed-valence TmSe because the direct contribution of the  $4f$  electrons to the chemical bonding is very small. From our work it has become evident which types of itinerant electrons play a role in mixed-valence compounds such as TmSe. Based on our results it is possible to improve the existing model Hamiltonians by including a more realistic description of the itinerant electrons which are responsible for all chemical effects; this will lead to better results for the structural dependence of the  $4f$  excitation energies. Finally, our calculations correctly relate the integral-valence-to-mixed-valence transition in Tm compounds to the closing of a gap between the  $f$  band and the conduction  $d$  band.

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