

SELF CONSISTENT GROUND STATE AND OPTICAL PROPERTIES OF THALLOUS HALIDES

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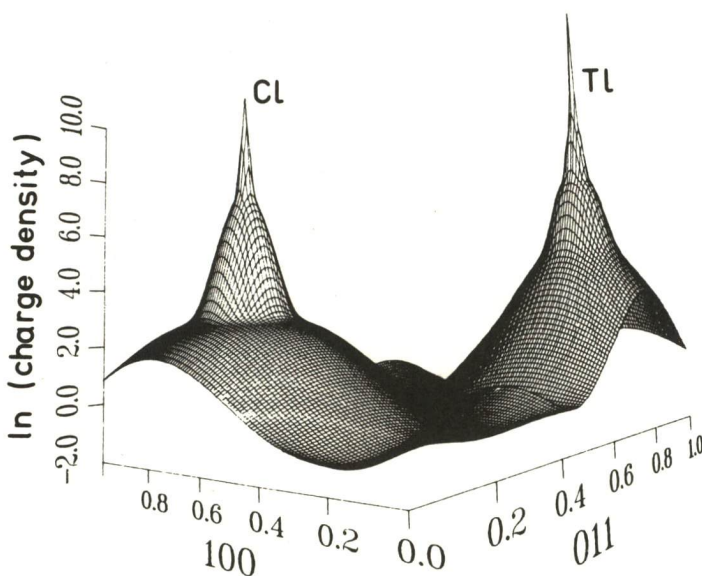
A first principles, self-consistent relativistic calculation of the electronic structure, density of states, equilibrium lattice constant, cohesive energy and compressibility for simple cubic TlCl and TlBr, and of the dielectric function of TlCl is presented.

I. Introduction

Ten-electron compounds such as TlCl and TlBr differ considerably in many of their physical properties from the more familiar eight-electron compounds such as Ge, GaAs, or ZnSe. Besides the general interest to understand the particular properties of this class of compounds, (as e.g. high ionic polarizability combined with an unusually small electronic energy gap, strong electron-phonon coupling, polymorphism etc.), there is another motivation for our work, namely: This is the first ab-initio calculation for a semiconductor with such high atomic number and ionicity and the first successful attempt to calculate the optical response of a semiconductor including many-particle effects on the same footing as the ground state properties.

II. Ground State

In the LDF-formalism [1] the ground state energy of a solid is a unique functional of the ground state charge density and given as a sum of kinetic, coulombic and exchange-correlation energies. We treated the latter following Hedin and Lundquist [2,3]. On the basis of a frozen-core approximation we used as trial functions $\text{Tl}^{+}6s$ and $\text{Cl}^{-}3p$ ($\text{Br}^{-}4p$) orbitals in a gaussian representation, thus forming the minimal basis set (MBS), and, by inclusion of $\text{Tl}^{+}6p$ orbitals, an extended basis set (EBS). The localization of these basis functions, which were explicitly orthogonalized onto all core orbitals, was varied to minimize the ground state energy as a functional of this localization, and in a further step as a function of the lattice parameter. Relativistic effects were included. Full self-consistency was obtained in the MBS. A resulting charge density is shown in Fig. (1).



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Fig. 1
Total charge density of TlCl: A uniform distribution of all electrons would yield $\ln(n) \approx 2.5$.

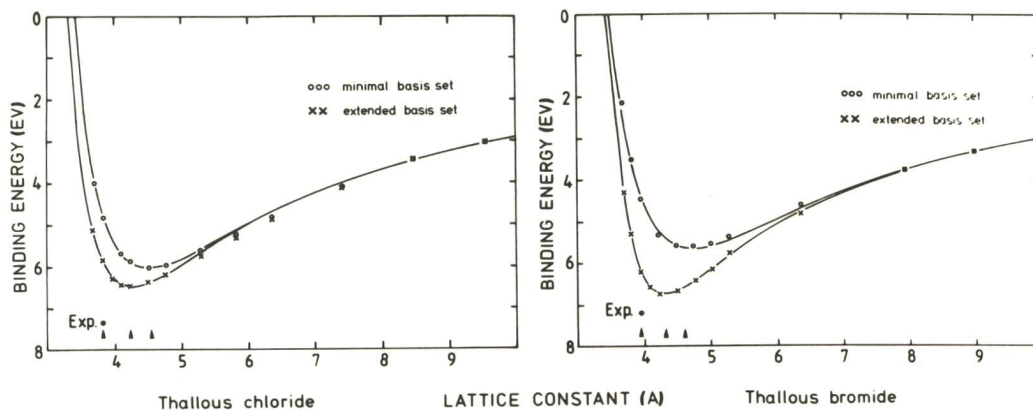


Fig. 2 Dependence of the total energy on the lattice parameter: Arrows indicate the equilibrium lattice constants in MBS, EBS, and experiment.

The ground state energy as a function of lattice parameter is given in Fig. (2), where the full lines represent interpolations of the calculated points with Born-Mayer like potentials. The inclusion of 6p-orbitals (EBS) yields a substantial improvement as concerns the calculated cohesive energy E_c , and the lattice constant a_0 , see table (1). Even the compressibility β of the thallous halides is reproduced by the calculation within a margin of less than 15% from the experimental value in the EBS.

Table 1 Ground state properties of thallous halides

TlCl			TlBr		
MBS	EBS	Exp	MBS	EBS	Exp
5.9	6.4	7.4	5.65	6.7	7.2
4.50	4.10	3.84	4.65	4.25	3.97
9.2	3.7	4.3	9.8	4.1	4.8
E_c [eV]					
a_0 [Å]					
β [10^{-12} cm ² /dyn]					

III. Band Structure

To calculate a quasi-particle spectrum from the LDF ground state one can solve the Dyson-equation for the one-particle Green's function by approximating the electronic self-energy in the same spirit as it is done in the ground-state formalism for the exchange and correlation energies. Starting from the self-consistent potential calculated in Section II by minimizing the ground state energy we calculated the energy bands with and without selfenergy corrections in the EBS and at the experimental lattice constant. The resulting band structures are shown in Fig. (3). They show that the influence of the self-energy corrections is small, thus reinforcing the usefulness of the one-electron picture. Moreover, they agree well with former calculations [4] and with experiment [5]. The agreement with experiment is even better in many respects than that of former calculations, which is the more satisfactory as no fitting parameter has entered our calculations.

The direct gap at the X-point of the Brillouin-Zone as well as the indirect X-R transition are smaller than the experimental values, a defect that can be cured at least to a great deal by going beyond the frozen-core approximation.

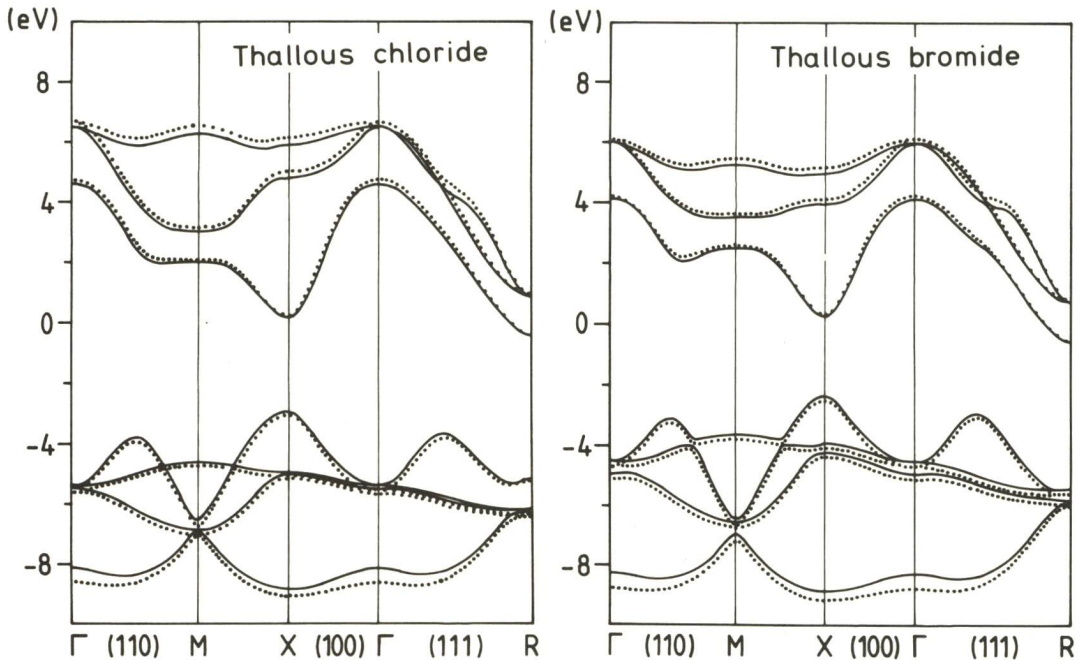


Fig. 3
Thallous halide bandstructures with
(full lines) and without (dotted lines)
selfenergy corrections

IV. Density of States

The most remarkable deviation of our calculation from former ones [4] is the width of the valence bands in TlCl and TlBr . Since our calculation is not based on a fit to optical (i.e. transition) data, but on a careful analysis of the ground-state, the results should be more trustworthy from the outset. As a careful re-analysis of photoemission data [6,3] and new measurements [7] have shown, the density of states of the valence bands calculated here is in convincing agreement with experiment, see Fig. (4).

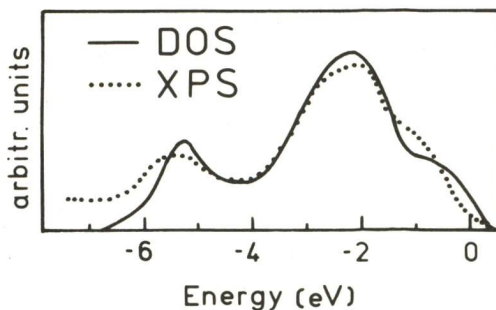


Fig. 4
Density of states and XPS-electron
density curves (from [7]) for TlCl

V. Optical Properties

To calculate the dielectric function $\epsilon(\omega)$ we used the approach of Hanke and Sham [8] with some modifications, the details of which are described in [9]. For simple cubic TlCl we started with the relativistic band structure and the EBS-wave functions in a Gaussian representation as described above. Inclusion of second nearest neighbours into the calculation of the transition matrix elements was proven to be sufficient for convergence of the Ehrenreich-Cohen [10] dielectric function, i.e. neglecting local-field and exchange corrections. Taking this convergence for granted for the many-body-approach, too, we ended up with a 367×367 matrix which had to be inverted to get the dielectric function including many-particle corrections. The exchange matrix elements were statically screened with $\epsilon(q) = \epsilon_{\infty} f(q)$, where ϵ_{∞} was determined self-consistently and $f(q)$ was taken from the Ehrenreich-Cohen dielectric function.

To confirm the consistency of the calculation, we have calculated the EC-dielectric function in current, and in density-representation. Deviations are negligible.

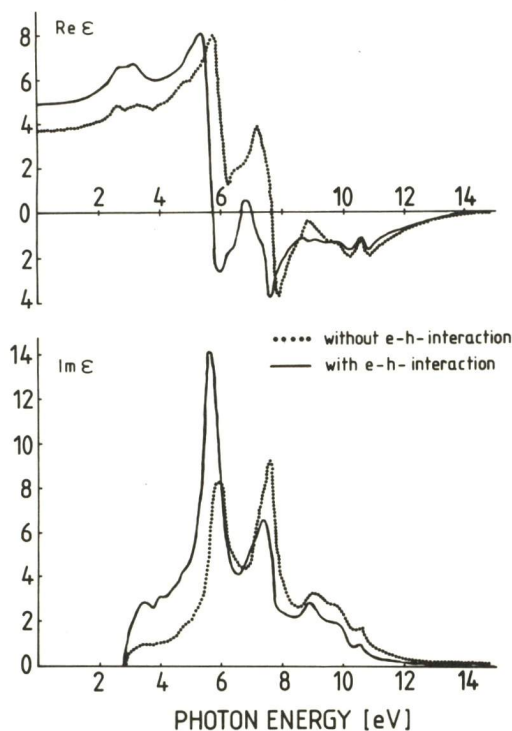


Fig. 5
Real and imaginary part of the TlCl-dielectric function with and without many body effects

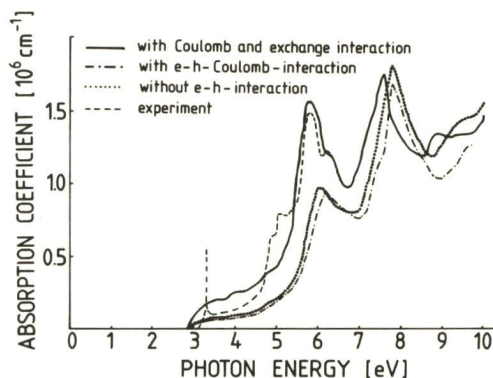


Fig. 6
Different approximations to the absorption coefficient of TlCl, experiment from [5]

The results of our calculations are shown in Fig. (5). They render the typical result, see e.g. [8], that many body corrections shift the optical spectrum to the low-energy side mainly by shifting oscillator strength. The agreement with experiment [5] of the self-consistently calculated spectrum including exchange and local-field corrections is convincing, see Fig. (6).

In conclusion we feel that the LDF-formalism and the approaches to treat many-body corrections to the ground state as well as to the electronic excitation spectrum have been shown to be appropriate in the comparatively hard test of substances with such high atomic number and strongly varying charge density.

VI. References

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