[4] R. J. Garber, G. P. Dolya, V. M. Kolyada, A. A. Molden, and A. I. Federenko, Pis'ma Zh. Eksp. Teor. Fiz. 7, 375 (1968) [JETP Lett. 7, 296 (1968)].

[5] K. Verghese, Trans. Amer. Nucl. Soc. 12, 544 (1969).

[6] R. F. Garber, V. S. Karasov, V. M. Kolyada, and A. I. Federenko, At. Energ. 28, 400 (1970) [Sov. At. Energy 28, 510 (1970)].

[7] T. S. Baer and J. N. Anno, J. Appl. Phys. 43, 2453 (1972).

[8] M. Kaminsky, J. H. Peavey, and S. K. Das, Phys. Rev. Lett. 32, 599 (1974).

[9] M. Kaminsky and S. K. Das, J. Nucl. Mater. 53, 162 (1974).

[10] R. Behrisch, Nucl. Fusion 12, 695 (1972).

[11] M. A. Kirk, T. H. Blewitt, A. C. Klank, and T. L. Scott, J. Nucl. Mater. 53, 179 (1974).

[12] R. Behrisch, R. Bahler, and J. Kalus, J. Nucl. Mater. 53, 183 (1974).

[13] S. J. Taimuty, Nucl. Sci. Eng. 10, 403 (1961).

[14] P. Sigmund, Phys. Rev. 184, 383 (1969).

[15] M. T. Robinson, J. Nucl. Mater. 53, 201 (1974).

[16] M. Guinan, J. Nucl. Mater. 53, 171 (1974).

[17] J. Weertman, to be published.

[18] J. D. Seagrave, "$D(d,n)He^3$ and $T(d,n)He^4$ Neutron Source Handbook," LASL Report No. LAMS-2162, 1958 (unpublished).

[19] R. L. Brodzinski *et al.*, to be published.

[20] M. Kaminsky and S. Das, J. Appl. Phys. 44, 25 (1973).

Electronic Band Structure, Bonding, and Ionicities of Polymorphous Thallous Halides

J. Treusch
Institut für Physik der Universität Dortmund, 46 Dortmund, Germany

(Received 20 January 1975)

An empirical linear-combination-of-atomic-orbitals energy-band model is described for simple-cubic and fcc TlCl, TlBr, and TlI which explains optical data and reproduces existent *a priori* band structures. This band model is used to discuss the type of bonding in the polymorphs, and to check the applicability for ten-electron systems of the Phillips–van Vechten dielectric theory of bonding.

The Phillips–van Vechten dielectric theory (PV theory) of bonding and ionicity[1] has undoubtedly been extremely successful in the field of eight-electron systems, ranging from tetrahedrally coordinated semiconductors, for which it had been primarily intended, to crystals as ionic as the alkali halides. This success initiated several attempts to extend this theory to more complicated compounds,[2] including those where d electrons play an important role, and even to ten-electron systems like the lead chalcogenides and thallous halides.[3]

Recent optical measurements and band-structure calculations on the polytypes of TlCl, TlBr, and TlI,[4] which can be grown in NaCl structure (fcc) as well as in their normal CsCl structure [simple cubic (sc)], yield an almost ideal opportunity to check whether these ten-electron compounds fit into the pattern of the PV theory. Moreover, a treatment of these rather simple systems may also help for a better understanding of other more complicated systems with a cationic s shell exceeding the rare-gas configuration.

The basic difference between the thallous halides and the alkali halides from our point of view is the fact that the anion s-type conduction band and the cation p-type valence band, which in the latter case form the average gap entering the PV theory, are both occupied in thallous halides. So, what can be used as an average gap of the thallous halides is actually the distance between the mixed s-p valence band and the p-type cationic conduction band. It is not at all clear from the outset whether this "cationic" gap reproduces chemical trends in the same sense as the "charge-transfer" gap of eight-electron systems normally does. Moreover, the s shell of the cation is very easily deformable, leading to anomalously high values of the static dielectric constant, ϵ_0, in all ten-electron compounds. This in addition may hinder a description in terms of the electronic dielectric constant, ϵ_∞, alone.[5]

To make possible a description of the thallous halides, which is unambiguous, simple, and shows the essentials of why the electronic structure is as it is, an empirical linear-combination-of-atomic-orbitals (LCAO) scheme has been developed.[6] This scheme reestablishes the band structures that have been calculated with the Korringa-Kohn-Rostoker (KKR) method for all six polymorphs and which are taken for granted since they explain optical data very satisfactori-

TABLE I. Parameters and results of the empirical LCAO model. d gives the bond length in Å; E_M is the Madelung energy; E_G is the experimental value of the gap energy (Refs. 4 and 7). $\Delta_{sp}{}^{\text{fit}}$ is used to fit the KKR band structures of Refs. 4 and 7; $\Delta_{sp}{}^{\text{theor}}$ is calculated from Eq. (1) and Ref. 8. The other parameters are described in the text.

	d	$-E_M$	E_G	Valence band $\Delta_{sp}{}^{\text{fit}}$	$\Delta_{se}{}^{\text{theor}}$	V_{ss}	V_{sp}	Conduction band E_{sp}	V_1	V_2	E_{av}	$\epsilon_\infty{}^{\text{theor}}$	$\epsilon_\infty{}^{\text{exp}}$
fcc TlCl	3.15	7.96	3.8	0.2	0.26	−0.1	1.3	8.6	0.25	1	8.5	4.0	
TlBr	3.28	7.646	3.4	0.8	0.90	−0.1	1.3	8.4	0.15	1	7.8	4.5	
TlI	3.47	7.225	3.0	1.8	1.75	−0.05	1.3	8.3	0.1	1	6.9	5.1	
sc TlCl	3.33	7.595	3.4	1.1	1.00	−0.35	0.51	8.3	2.25	0.14	7.5	5.2	5.0[a]
TlBr	3.44	7.353	3.0	1.55	1.50	−0.3	0.56	8.1	2.15	0.14	6.9	6.0	5.6[a]
TlI	3.63	6.97	2.85	2.5	2.28	−0.2	0.5	7.9	2.0	0.1	6.0	7.0	7.0[b]

[a] Low-temperature values of Ref. 9.

[b] Taken from Ref. 3.

ly.[4,7]

The following parameters are necessary in the LCAO scheme to reproduce the KKR band structures with an overall accuracy of 0.3 eV: (1) The distance Δ_{sp} between the cationic s-type and the anionic p-type valence bands, and the distance E_{sp} between the Tl s valence band and the Tl p conduction band. Both of these parameters are defined as differences between the center-of-mass energies (averaged over the Brillouin zone) of the respective bands. These are equal to the k-independent part of the corresponding diagonal matrix elements of the LCAO Hamiltonian. (2) The bond strength V_{sp}, which broadens the mixed s-p valence band without shifting its *common* center of mass. (3) The cationic overlap between next-neighbor cations, V_{ss}. (4) Two conduction-band parameters V_1 and V_2, describing diagonal p-p overlap between next and second-nearest Tl neighbors. The anion s valence band lies about 10 eV below the top of the valence band and is not regarded here.

An optimum fit was obtained with the parameters given in Table I; a graph of this fit is shown in Fig. 1 for fcc and sc TlCl as an example.

As it turns out, Δ_{sp} is, within an 0.1 eV accuracy, given by the simple equation

$$\Delta_{sp} = E_p{}^{\text{free anion}} - E_s{}^{\text{free cation}} + 2E_{\text{Madelung}} \tag{1}$$

for all six polymorphs, where the free-ion eigenvalues are calculated with Liberman's program[8] using a Kohn-Sham exchange potential. V_{ss} is small and sensitively dependent on the cation-cation distance, which is larger in the fcc lattice than in the sc lattice; the s-p bond is rather insensitive in a given structure, but considerably stronger in the fcc than in the sc crystals. The conduction-band width decreases, too, with increasing cation-cation distance, whereas the so-called cationic gap, E_{sp}, is almost constant for all six polymorphs, namely, about 8 eV. The conduction-band spin-orbit splitting is 2.3 eV in all cases, whereas the valence-band spin-orbit splitting is 0.1, 0,5, and 1.2 eV for TlCl, TlBr, and TlI, respectively, in either structure and at $\vec{k} = 0$.

Three main conclusions can be drawn from this empirical band scheme: (I) The position in k space of the direct energy gap is uniquely determined through the nearest-neighbor geometry of the crystal, namely, for eightfold coordination it is situated at the end of the ⟨100⟩ axis, and for sixfold coordination at the end of the ⟨111⟩ axis. (II) The s-p bond is strengthened by a factor of about 2.5 for the fcc structure as compared to the sc structure. In addition the intra-valence-band

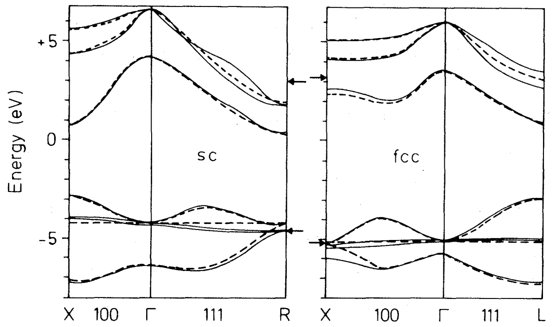

FIG. 1. Electronic band structure of sc and fcc TlCl as calculated with the KKR method (Refs. 4 and 7; full lines) and with the empirical LCAO scheme (dotted lines). The spin-orbit splitting of the *valence band* is neglected in the LCAO band structure for sake of clarity. Arrows indicate centers of mass of conduction and valence bands, respectively.

distance Δ_{sp} decreases by about 0.8 eV for all three salts because of the increased Madelung energy of the fcc phases. (III) The average electronic gap, which I defines as

$$E_{av}=E_{sp}-\tfrac{3}{4}\Delta_{sp}, \tag{2}$$

i.e., the distance between the centers of mass of valence and conduction bands, is increased by about 1 eV for the fcc crystals as compared to the sc crystals. The electronic dielectric constants are calculated from these average gaps with Penn's formula (see Ref. 1),

$$\epsilon_\infty = 1+(\hbar\omega_p/E_{av})^2 C,$$

where ω_p is the plasma frequency and the correction factor C, which is close to unity in all cases, is taken from Levine.[3] The results for ϵ_∞ are given in Table I and are in convincing agreement with experimental values for the sc case, where these are known. This agreement is taken as strong support for the definition of E_{av} which neglects variations in transition matrix elements.

Now the question shall be discussed how these conclusions compare with PV theory as it has been applied for sc thallous halides by Levine.[3] We will use the formulas [Eqs. (9)–(12) of Ref. 3]

$$\begin{aligned} E_h &= 39.74/d^{2.48}\ \text{eV},\\ C &= 14.4b\exp(-k_s r_0)\Delta Z/r_0\ \text{eV},\\ E_{av}^2 &= E_h^2+C^2, \end{aligned} \tag{3}$$

and

$$f_i = C^2/(E_h^2+C^2),$$

for the homopolar, heteropolar, and average gaps, respectively, and for the ionicity f_i. d is the bond length to be taken from Table I, $\exp(-k_s \times r_0)$ is the Thomas-Fermi screening factor calculated for ten valence electrons, the charge difference, ΔZ, equals 4, and r_0 equals $d/2$. The prescreening factor b should be 3.39± 18% for fcc crystals.[3] Taking these values, which are proposed by Levine for a generalized description of ionicities, we end up with average gaps of 6, 5.5, and 4.7 eV for fcc TlCl, TlBr, and TlI, respectively, which severely differ from the values in Table I.[10] To reproduce these values a prescreening factor as large as 5 would be necessary, which falls far off the range of 3.39± 18%. A more physical assumption would be to change the charge difference ΔZ from 4 to a value close to 5 (i.e., not all of the Tl valence electrons are equally effective). This would yield $b\approx 4$, close to the value for, e.g., RbCl, which is 4.16.[3] Moreover, such an assumption would also improve the situation in the sc case, lowering the b values of the sc thallous halides given by Levine to approximately those of the cesium halides.[3] So, a reasonably consistent description of the *electronic* dielectric constant along the lines of the PV theory seems to be possible for the thallous halides, although one more open parameter, namely ΔZ, has to be fitted.

On the other hand, the ionicities, f_i, to be extracted from this treatment differ between the sc and fcc phases by less than 1%. This equality of ionicities does not explain the apparent differences of the two structural modifications, e.g., the exciton binding energy, which is 10 times larger in the fcc phase than in the sc phase.[4]

To qualify the statement that fcc thallous halides are more covalent in character than sc thallous halides, a description with an average electronic gap obviously is insufficient. Semiquantitative conclusions, however, are possible concerning the ratio $\epsilon_0/\epsilon_\infty$, which seems to be a better means to at least qualitatively describe ionicity in cases where ionic and electronic properties are as closely connected as they are in the thallous halides. From the Szigeti formula[9]

$$\epsilon_0=\epsilon_\infty+\tfrac{4}{9}(N/\mu)(\epsilon_\infty+2)^2 e^{*2}\omega_T^{-2}, \tag{4}$$

we concluded[4] that ϵ_0 should be of the order of 10 in fcc TlCl and TlBr as compared to about 35 in sc TlCl and TlBr. Here μ denotes the reduced ionic mass, N the number of molecules per unit volume, e^* the effective ionic charge, and ω_T the transverse phonon frequency. This strong decrease of the static screening together with the slight decrease of ϵ_∞ explained the large excitonic binding energy very well.[4] If we use the same parameters as used in formula (4) to calculate the bulk compressibility with a second Szigeti formula,[9]

$$\beta^*=\frac{3}{N\mu r_0^2}\,\frac{\epsilon_\infty+2}{\epsilon_0+2}\,\omega_T^{-2}, \tag{5}$$

we find good agreement between β^* and the experimentally determined compressibility β_{exp} of sc TlCl and TlBr, namely, $\beta^*\approx 1.15\beta_{\text{exp}}$. In addition we calculate from (5) $\beta_{\text{fcc}}^*\approx 2.5\beta_{\text{sc}}^*$ for TlCl as well as for TlBr. This drastic increase in compressibility has two important consequences. The repulsive part of the total cohesive energy[11] is increased by a factor of 2, showing a value of +1.4 eV/mol. Thus the absolute values of the cohesive energy of the fcc crystal, which otherwise would be higher than those of the sc crystals, are lower than these values. This agrees with experience, since sc TlCl and TlBr are the normally stable phases. The second consequence is a lowering of the longitudinal-phonon frequency, which together with the increase of ω_T (due to increasing bond strength) is necessary to fulfill the Lyddane-Sachs-Teller relation: For fcc thallous halides the ratio $\epsilon_0/\epsilon_\infty$ lies between 2 and 3, whereas for sc thallous halides this ratio is almost 7[9]; thus the ratio ω_L/ω_T should range between 1.4 and 1.8 (fcc) instead of being close to 2.6 (sc). A detailed calculation of the phonon frequencies of fcc thallous halides has to be waited for; an experimental determination is lacking too. From the arguments and experiments known up to now, however, it seems justified to ascribe to the fcc thallous halides a noticeably higher degree of covalency than to the sc ones.

In conclusion, I feel, that a straightforward application of the PV theory to ten-electron systems, whereas it may yield reasonable results for the electronic dielectric constant, is doubtful as far as ionicities are concerned. It is hoped that this work on the thallous halides will be a stimulus for examination or re-examination of other ten-electron systems, such as lead chalcogenides, or similar systems, e.g., lead and bismuth halides.

The author is indebted to W. Staude, H. Overhof, and K. Heidrich of many helpful discussions.

---

[1] E.g., J. C. Phillips, Phys. Rev. Lett 20, 550 (1968), and Rev. Mod. Phys. 42, 317 (1970), and *Covalent Bonding in Crystals, Molecules, and Polymers* (Univ. of Chicago Press, Chicago, Ill., 1969); J. A. van Vechten, Phys. Rev. 182, 891 (1969), and 187, 1007 (1969).

[2] See, e.g., B. F. Levine, Phys. Rev. B 7, 2591, 2600 (1973). A large amount of literature in this field is quoted here.

[3] B. F. Levine, J. Chem. Phys. 59, 1463 (1973); D. Schiferl, Phys. Rev. B 10, 3316 (1974).

[4] K. Heidrich, W. Staude, J. Treusch, and H. Overhof, Phys. Rev. Lett. 33, 1220 (1974), and to be published.

[5] The work of S. H. Wemple and M. Di Domenico, Phys. Rev. B 3, 1338 (1971), will not be helpful for the same reason, since it explains the behavior of the *electronic* dielectric constant alone. It should be noticed, however, that, if the dispersion energy E_d does not change between the fcc and sc phases, then the value of β, as defined by Wemple and Di Domenico, would take on the "covalent" value 0.35 in the fcc case as compared to the "ionic" value 0.27 for the sc case, as a consequence of lowering the coordination number.

[6] An extended description of this LCAO model will be given by J. Treusch, to be published.

[7] H. Overhof and J. Treusch, Solid State Commun. 9, 53 (1971); R. Z. Bachrach and F. C. Brown, Phys. Rev. 81, 818 (1970).

[8] D. A. Liberman, D. T. Cromer, and J. T. Waber, Comput. Phys. Commun. 2, 107 (1971).

[9] R. P. Lowndes and D. H. Martin, Proc. Roy. Soc., Ser. A 308, 473 (1969).

[10] For sc thallous halides Levine's calculated average gaps (Ref. 3) are in good agreement with this paper's values, the maximum deviation being smaller than 0.6 eV. This is not surprising, since they are derived from experimental values of ϵ_∞.

[11] E.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), 3rd ed., pp. 89–98.

Optically Induced Localized Paramagnetic States in Chalcogenide Glasses

S. G. Bishop, U. Strom, and P. C. Taylor
Naval Research Laboratory, Washington, D. C. 20375

(Received 7 April 1975)

Optically induced ESR and absorption due to localized paramagnetic states in the forbidden gap have been observed in several semiconducting chalcogenide glasses below ~15 K. Analysis of the ESR spectra indicates that these centers are holes localized on chalcogens and are not directly associated with impurities.

It has long been argued that there exist in the forbidden energy gaps of amorphous semiconductors localized electronic states which might be attributable to dangling bonds, impurities, or other defects in the structure of the disordered solid.[1] Various studies of the optical[2] and electronic[3] properties of chalcogenide glasses have been interpreted in terms of such localized gap states, and densities of localized states in the range 10^{17} to 10^{19} $\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$ have been inferred from the experimental results. The most contradictory experimental result concerning the exis-