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BAND STRUCTURE DETERMINATION BY THE GREEN'S FUNCTION METHOD

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Summary. — Recent work on band structure calculations shows that the Green's function method (KKR) is appropriate not only for metals but also for semiconductors such as selenium, tellurium, and zinc sulphide. The method belongs to the so called « first-principle » methods, in contrast to the interpolation schemes (based e. g. on a pseudopotential). Distinguishing features are its mathematical rigor and rapid convergence. The only shortcoming is that the method only applies to a muffin-tin potential. But since the bands do not depend strongly on the special form of the assumed potential, one should expect reliable results if the real potential is not very far from spherical symmetry. The energy bands calculated for Se, Te, and cubic ZnS fit experiments satisfactorily and are comparable with pseudopotential results. Moreover they are even better than those obtained by tight-binding calculations. That is very promising since there is only one fitting parameter, against e. g. six in the interpolation scheme used in the work on ZnS. Therefore KKR-calculations are an excellent starting point for energy band analysis specially since they require few experimental data. A recent modification of the Green's function method includes spin-orbit coupling from the very beginning.

Résumé. — Les derniers travaux sur la détermination théorique de la structure des bandes montrent que la méthode dite de la fonction de Green (K K R) n'est pas seulement applicable aux métaux, mais aussi à des semiconducteurs tels que Se, Te et ZnS. Cette méthode fait partie des méthodes dites de « first principles », en contraste avec les schémas d'interpolation (basés par exemple sur le pseudopotential). Les faits qui l'en distinguent sont la rigueur mathématique et la rapide convergence. Son seul désavantage réside dans le fait qu'elle ne s'applique qu'au « muffin-tin » potentiel. Mais si la structure de bandes ne dépend pas excessivement du potentiel utilisé et si le véritable potentiel ne dévie pas beaucoup de la symétrie sphérique, on doit pouvoir obtenir des résultats satisfaisants. Les bandes d'énergie calculées pour le Se, Te et le ZnS satisfont aux résultats expérimentaux et sont comparables aux résultats obtenus par la méthode dite du pseudo-potential. D'autre part, ils sont meilleurs que ceux obtenus par la méthode dite du « tight-binding ». Ceci est très prometteur, surtout si l'on remarque qu'il suffit ici d'un seul paramètre pour expliquer l'expérience, au lieu de six par exemple dans le schéma d'interpolation appliqué à ZnS. De tels calculs (K K R) peuvent être de précieux points de départ pour l'étude des bandes d'énergie, surtout dans les cas où il n'existe que peu de résultats expérimentaux. Une modification de la méthode de la fonction de Green comprenant le couplage spin-orbite dès le début de la théorie a été développée récemment.

Among the methods used in band structure calculations three groups can be distinguished,

- 1) methods that try to get self-consistent solutions of the Schrödinger equation for the one-electron periodic potential problem
- 2) methods that use ad hoc potentials, and
- 3) methods that use experimental data to fit unknown parameters in interpolation schemes, i. e. to get the band structure in full k -space from known energy values in certain symmetry points.

The self-consistent methods are of course the only ones that can predict the band structure of a given solid without any experimental knowledge. Among

these methods the OPW-method seems to be most suitable. But until now it has never been possible to carry out completely self consistent band structure calculations for the following reasons : *a*) The calculations are extremely long. *b*) The results depend strongly on the accuracy of some orthogonalization integrals. *c*) Furthermore they depend on the validity of some physical assumptions (e. g. core-shift, correlation effects). For this reason some fitting parameters have to be introduced *a posteriori* in order to avoid bad agreement between theory and experiment [1, 2, 3, 4].

Among the ad hoc potential methods the APW-method (augmented plane waves) [5] and the KKR-method (Green's function method by Korringa [6],

Kohn and Rostoker [7]), share the best reputation. Both methods use a spherical potential around each lattice point and a constant potential outside these spheres (muffin-tin potential). Recently they have been proved to be almost equivalent. The disadvantage of using an idealized potential is balanced by many advantages. The theory is transparent, the numerical calculations are fewer than in a self-consistent theory, and there is only one free parameter namely the value of the constant potential outside the spheres.

The basic disadvantage of the interpolation schemes is the necessity to know the band structure at certain points in the Brillouin zone *a priori*. Experimental values of optical transitions can help if available, but wrong attachment of these values to critical points in the Brillouin zone leads to wrong band structures [3, 4]. Some approximations in the physical assumptions [2], which do not necessarily hold for semiconductors as they do not hold e. g. for transition metals (e. g. replacement of the non local dynamic repulsive potential by a local potential, (overlapping) spherical potential around the atoms, etc.), lead to some restrictions. Thus by the pseudopotential interpolation scheme [8] no d-bands can be described, whereas the tight-binding interpolation scheme [9] can give no « free electron »-bands. The combined interpolation scheme of Mueller [10] seems to overcome these difficulties. Apart from these points especially the pseudopotential method has turned out to be a very strong tool for rapid and extensive band structure calculations in relatively good known solids [11]. It is the only method up to this day which almost gives the energy bands not only at symmetry lines in the BZ, but at general points in k-space as well.

The APW - or the KKR-method will be chosen in two cases :

- 1) If the muffin-tin potential assumption is a good approximation, as e. g. in solids with a high coordination number, especially in cubic metals with Bravais lattices. Here excellent results have been obtained [12, 13, 14, 15].

- 2) If no (or only tentative) experimental data exist for a solid, the muffin-tin methods are a good starting point for band structure calculation.

APW - and KKR-methods have been proved to be closely related [16, 17, 18, 19]. But the KKR-method seems to be advantageous in many respects. The convergence relative to the l -summation is better than in the usual form of the APW-method as was shown by calculations on cubic ZnS [20, 21]. The solutions are continuous with continuous derivatives at the surface

of the muffin-tin spheres [22]. The greatest advantage as to the numerical calculations is a complete separation of the influences that the lattice symmetry and the potential have on the band structure. Thus the so called « structure constants » (that need by far the greatest amount of computing time) can be calculated once and for all for a given crystal or group of crystals, and the potential used can then be changed very easily. The spin-orbit coupling, the relativistic Darwin term and the mass-velocity correction can be treated separately [23]. Thus the influence of different assumptions on the results can be investigated during the calculations. For this treatment the relativistic Pauli equation must be used. Beginning with the Dirac equation leads to almost the same results in the frame of the usual approximations but without the possibility to separate the different terms [24, 25].

The application of the KKR-method to semiconductors has been extensively investigated at the first time by Sandrock and Treusch for the band structure of Se and Te [22] (besides some tentative work on Ge by Segall [26]). Other work concerning these two semiconductors up to this time had been based upon the tight-binding method. There, atomic orbitals have been used as trial functions [27]. Taking into account only nearest neighbours, one hurts the Bloch condition severely and gets the band structure along the hexagonal A -axis only. These restrictions throw some doubt on the Se-results of Olechna and Knox [28]. Results that are more complete have been obtained by Hulin [29, 30] for Te. He takes into account second nearest neighbours too, thus gets the band structure for the four main symmetry axes and finds the gap to be situated in the corner of the Brillouin zone (H). In contrast to Olechna and Knox who start with a definite potential and fit by just changing the value of the exchange potential, Hulin's calculation is more empirical. Unfortunately, he fits effective masses instead of energy values. That leads to an energy gap which is ten times larger than the experimental value. Other work (done by Hulin [30] to show the suitability of the tight-binding method in the case of Te) gives reason to conclude that the muffin-tin approximation will exhibit good results in Se and Te, since the valence electrons are concentrated near the ion cores of the lattice atoms.

The KKR-calculations for Se and Te give the following picture (Fig. 1, 2) : the valence and conduction band originate from the p-terms of the lattice atoms and do mix only to a small degree with the free electron terms. This result shows that pseudopotential calculations are not as appropriate as e. g. tight binding calculations. The energy gap according to the

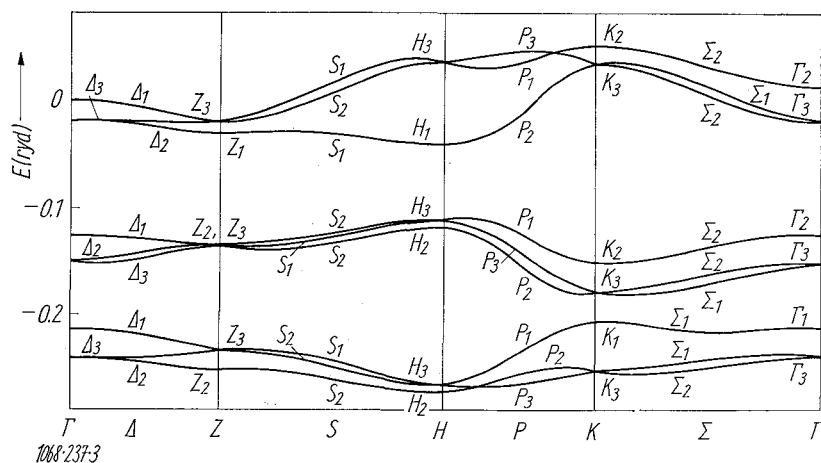


FIG. 1. — Band structure of Se in accordance to [22].

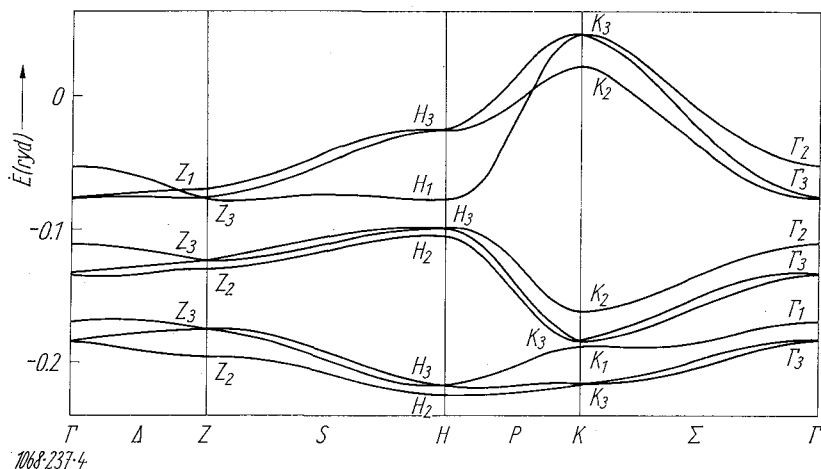


FIG. 2. — Band structure of Te [22].

KKR-calculations lies also in the point H for both Se and Te and is of the right order of magnitude. Optical transitions and the 11μ band found experimentally can be described correctly. The pressure dependence of the energy gap in Se can be explained quantitatively. Especially this last result, which can only be won by taking the full lattice structure into account (that means not only neighbour atoms in the chains but neighbouring chains too), shows the superiority of the KKR-method. At first glance spherical potentials seem to be a bad approximation to the chain structure of Se and Te, but the proximity of the spheres in the chains and the relatively great distance between the chains gives the necessary anisotropy of the chemical bond. Pseudopotential calculations by Beissner [31] are restricted to the Δ -axis. Therefore, and by the reasons stated above they seem to be unreliable.

After our encouraging results, we investigated the application of the KKR-method to semiconductors with zinblende structure. As in the case of Se and Te the spheres fill only about a third of the space. Thus the assumption of a muffin-tin potential is incisive. Nevertheless, the muffin-tin approximation seems justified if by a heteropolar bond the electron bridges are polarized. As our first example, we chose cubic ZnS. For the potential inside the spheres the first consistent atomic potentials of Herman and Skillman [32] were used, although a more ionic potential would seem to be more nearly adequate; but the results do not depend strongly on the exact form of the potential inside the spheres. Changing, for example, the potential in the region of the sphere radius by as large an amount as 15 eV does not essentially change the resulting band structure. Tab. 1 shows the resulting energy values [21]. The value of the potential outside

transition	Eckelt [21]	exp.	C & B (11)
$\Gamma_{15}-\Gamma_1$	3.7	3.7 (3.8)	3.7
$\Gamma_{15}-L_1$	5.3		5.3
$\Gamma_{15}-X_1$	5.8		5.2
$\Gamma_{15}-\Gamma_{15}$	9.0	8.4	8.9
X_5-X_1	7.2	7.03 (6.8)	6.7
X_5-X_3	7.5	7.35 (7.3)	7.5
X_1-X_3	0.3	0.32 (0.5)	0.8
L_3-L_1	5.9	5.82 (5.9)	5.8
L_3-L_3	9.9	9.65 (9.5)	9.2
m_e^*	(0.35-0.40) m_0	(0.39 \pm 0.01) m_0	< 0.35 m_0

TABLE 1. — Energy splittings of cubic ZnS in eV. The experimental values are measured by Cardona and Harbeke (*Phys. Rev.*, 1467, 137 A, 1965), except the transition $\Gamma_{15}-\Gamma_{15}$ which was measured recently by Baars (to be publ.). The values given in brackets are those that were fitted by C & B. They originate from the same experiment, but were extrapolated to $T = 0$. m_e^* was measured by H. Kukimoto et al. *Phys. Letters*, 1965, 19, 551.

the spheres was obtained by fitting the experimental value of the energy gap (optical transition $\Gamma_{15}-\Gamma_1$). The other optical transitions known from experiment are in good accordance with the respective energy differences of the theoretical band structure. The results are very similar to those obtained by Cohen and Bergstresser [11] who used the pseudopotential method with six fitting parameters. In contrast to these results, our calculations give the lower d-bands too. More details will be published elsewhere [21].

The tentative results about the energies in the point Γ of the Ge band structure obtained by Segall [26] from the KKR-method are not very promising. We are investigating the question of whether these results can be improved or whether the KKR-method fails if applied to such a covalent crystal. Work is in progress to include spin-orbit coupling and relativistic effects into the band structure of Se and Te.

The results described above are very encouraging since they demonstrate the following facts : 1. the KKR-method is able to yield quantitative results also for semiconductors, if the muffin-tin approximation is not too far from nature ; 2. the method is able to exhibit bands originating from atomic levels as well as free-electron bands, that means, it can be used to start band calculations in a special case and to decide what kind of interpolation scheme is suitable if one wants to know the energy throughout the Brillouin zone ; 3. the method is able to take into account rela-

tivistic effects from first principles and separately without enlarging the computational effort essentially.

Hence it seems promising to further investigate the KKR-method : to extend it, for example, by parameterization (as proposed by Heine) in order to get a semiempirical scheme that shares the advantages of the original method and those of an interpolation scheme, and to use it in cases, where self-consistent calculations are too extensive and interpolation schemes are impossible due to a dearth of experimental data.

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DISCUSSION

F. GAUTIER. — 1) V_0 est-il ajusté à l'expérience pour Se ?

2) Comment pouvez-vous représenter la variation de la structure de bandes (en méthode KKR) avec la distance entre les chaînes ?

O. MADELUNG. — 1) Oui, mais un ajustement total n'est pas possible (voir TREUSCH et SANDROCK, *Phys. Stat. Sol.*, 1966, **16**, 487).

2) Comme la méthode KKR est basé sur l'incorporation de *toute* la symétrie dès le début des calculs, une nouvelle détermination des bandes d'énergie en fonction de la distance entre les chaînes est facile, si l'on a déterminé les « structure constants » respectifs.

AMAR. — Is there any labor reduction in the determination of the KKR structure constants due to the chain structure of Te and Se ?

O. MADELUNG. — There is the usual reduction due to symmetry arguments, but the latter hold only for the diagonal structure constants. The non diagonal structure constants which appear, since we have no Bravais lattice in the case of Se and Te, are rather laborious to evaluate.

D. CURIE. — Is it possible to define some kind of effective charge for the zinc and sulfur ions in zinc sulfide, as a result from your calculations.

O. MADELUNG. — No. As a first approximation we used for our calculations the self-consistent atomic potentials of Herman and Skillman, without taking into account the ionicity of the chemical bond in cubic ZnS. As a second approximation one should use more ionic potentials and look if the results are changed essentially. But from our results we do not expect this to be the case.
