FIG. 2. Phonon dispersion curves in the [110] direction at a specific volume of 21.5 cc/mole. The solid curves are results of this paper, the dashed curves are computed from the theory of Ref. 7.

agreement. However, the calculated phonon energies differ significantly near the edge of the Brillouin zone. These results also obtain at other densities.

We feel that the theoretical approach outlined here offers a unified method of treating both highly anharmonic and slightly anharmonic systems by the expansion of the potential in general three-dimensional orthogonal polynomials or three-dimensional Hermite polynomials, respectively. In addition, the latter expansion has definite advantages over the conventional Taylor series expansion,[10] although the mathematical techniques of II are required to perform it. In contrast with the theories of Refs. 6 and 7, one is provided here with a clear-cut

procedure for extending the calculation since the orthogonal polynomials provide a complete set of wave functions so that perturbation theory can be used. Thus, one could expect to obtain an improved value of $E_0$ and to calculate phonon lifetimes.

The author has enjoyed discussing various aspects of this work with N. S. Gillis, N. R. Werthamer, W. J. Mullin, and L. H. Nosanow.

[1]T. R. Koehler, Phys. Rev. Letters 17, 89 (1966); this paper will be referred to as I.

[2]M. Born, in Festschrift zur Feier des zweihundertjährigen Bestenhens der Akademie der Wissenschaften in Gottingen. I. Mathematisch-physikalische Klasse (Springer-Verlag, Berlin, 1951), p. 1; D. J. Hooton, Phil. Mag. 46, 422 (1955).

[3]T. R. Koehler, Phys. Rev. 144, 789 (1966); this paper will be referred to as II.

[4]One constructs these wave functions by multiplying $|0\rangle$ by three-dimensional polynomials in the $q_i^\alpha$ which are products of Hermite polynomials in the normal coordinates $Q_k^\alpha$.

[5]When $f = 1$ this process recovers the traditional harmonic oscillator wave functions.

[6]L. H. Nosanow, Phys. Rev. Letters 13, 270 (1964); Phys. Rev. 146, 120 (1966).

[7]L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters 15, 618 (1965).

[8]N. G. van Kampen, Physica 27, 783 (1961).

[9]J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. 154, 175 (1967).

[10]For example, in perturbation theory, the $n$th term in the expansion of the potential has matrix elements only between states in which the total number of phonons is $n$ so that ground-state expectation values of higher order terms are eliminated.

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## BAND STRUCTURE OF CUBIC ZnS (KORRINGA-KOHN-ROSTOKER METHOD)

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Calculating the band structure of semiconductors crystallizing in the diamond or ZnS structure is a very interesting but also a difficult problem. Self-consistent calculations as performed by Herman[1] are extensive and until now only completed for Ge, Si, and grey tin (a perturbation calculation had to be added a posteriori). Results obtained with the aid of the pseudopotential-interpolation scheme have been published for 14 semiconductors by Cohen and

Bergstresser[2] (hereafter referred to as CB). But in spite of the striking success of this paper, the method is not fully satisfactory, since it is an empirical one and depends on a great deal of experimental data which must be interpreted properly.

To adopt a middle course—not as extensive as orthogonalized-plane-wave self-consistency but starting nearly from first principles—we undertook an application of the Green's func-

tion method [Korringa, Kohn, and Rostoker (KKR)] to semiconductors.[3] The main interest of the present work was to test the accuracy of the KKR method by applying it to a well-known semiconductor. ZnS served as an example since enough experimental information[4] and a well-fitted theoretical band structure[2] were available, thus enabling us to check our results. We are well aware of the shortcomings of this method which are due to the use of a muffin-tin potential. But, on the one hand, the band structure seems not to be influenced strongly by the special form of the assumed potential, a result that came out of our calculations and that was suggested by several authors (see e.g., Phillips[5]). On the other hand, the type of binding is partly ionic in ZnS; i.e., the muffin-tin potential is not so far from nature as, e.g., in diamond. Augmented-plane-wave (APW) calculations on ZnS[6] yielded results that were in qualitative but not in quantitative agreement with experiment. The KKR method, although related to the APW method, seems to have some advantages: E.g., there is better convergence as to the $l$ summation (we included $l = 2$), the wave function is continuous with continuous derivatives, potential and structure are clearly separated in the resulting secular determinant. Moreover the KKR method had already given good results for the hexagonal semiconductors Se and Te.[3]

We used a potential $V_1(r)$ (Fig. 1) that was built up by superimposing self-consistent atomic potentials.[7] The radii $R_{Zn} = 2.16r_B$ and $R_S = 2.27r_B$ were determined by the point of zero slope of $V_1(r)$. The only free parameter, namely, the constant potential outside the muffin-tin spheres was adjusted to $V_0 = -1.364$ Ry in

order to fit the experimentally measured energy gap. The calculated band structure (Fig. 2, Table I) was in astonishingly good agreement with experiment[4] and there was a striking resemblance to the results of CB. That is a proof of these results as well as a proof of the fact that the KKR method is a very powerful tool also in calculating band structures of semiconductors. Fitting the value of just one transition gives the values of six transitions more and the electron effective mass[8] with an accuracy comparable with or even better than that obtained by CB who used six parameters to fit experiment.[9] Moreover, while the $d$ bands cannot be produced by a pseudopotential calculation, they are given in our model and are in quite good agreement with experiment.[4,10]

Changing the potential as depicted in Fig. 1 $[V(r) = V_2$ with $V_0 = -0.594$ Ry$]$ does not change any transition by more than 5%. The bad agreement of the $\Gamma_{15}$-$\Gamma_{15}$ transition which is found in our calculation and by CB may be due to the assumption of a spherically symmetrical potential. A hint in this direction was also given by Herman,[1] who found the corresponding levels in Si and Ge about 0.5 eV below those coming out of pseudopotential calculations.[2]

Our results show that the KKR method can serve as an excellent starting point for band calculation if self-consistent calculations are too extensive or if there are few experimental

FIG. 1. Qualitative picture of the potentials used to calculate the ZnS band structure.
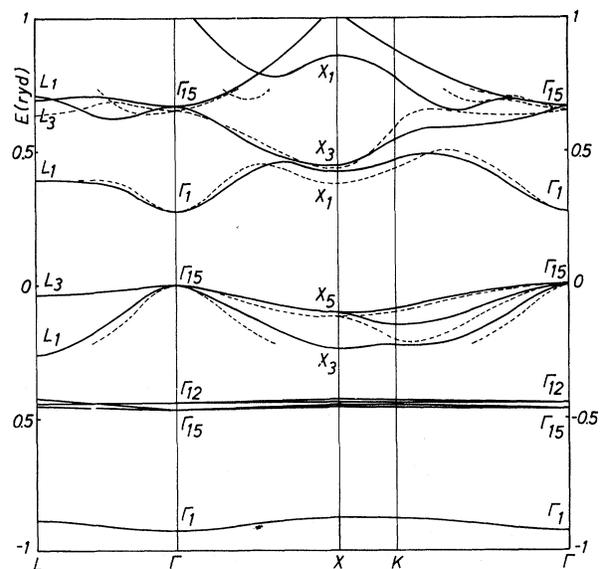
FIG. 2. The band structure of cubic ZnS as calculated by the KKR method and the results of Cohen and Bergstresser[2] (dashed lines).

Table I. Energy splittings (in eV) and effective electron mass of cubic ZnS as calculated by the KKR method and by CB in comparison with the experimental values found by Cardona and Harbeke,[4] by Baars,[a] and by Kukimoto.[b] The values given in parentheses are those that were fitted by CB. They originate from the same experiments but were extrapolated to $T = 0$. The lattice constant used in our calculation as well as by CB is related to room temperature.

| Transition | KKR | Experiment | CB[c] |
|---|---|---|---|
| $\Gamma_{15}$-$\Gamma_1$ | 3.7 | 3.71 (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[a] | 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 |
| $m_e{}^*$ | $(0.35-0.40)m_0$ | $(0.39 \pm 0.01)m_0$[b] | $<0.35m_0$ |

[a]H. Gobrecht and J. Baars, to be published.
[b]H. Kukimoto et al., Phys. Letters 19, 551 (1965).
[c]Cohen and Bergstresser, Ref. 2.

data. Since the method is able to exhibit bands originating from atomic levels as well as free-electron bands, one can use it to decide what kind of interpolation scheme is suitable if one wants to know the energy throughout the Brillouin zone. Moreover, the KKR method (like the APW method) has been modified to include spin-orbit coupling and relativistic effects (see, e.g., Treusch and Roessler[11]). So we hope that this method will be helpful in semiconductor research as it was in the theory of metals.

[1]F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, J. Phys. Soc. Japan Suppl. 21, 7 (1966).
[2]M. L. Cohen and M. H. Bergstresser, Phys. Rev. 141, 789 (1966).
[3]J. Treusch and R. Sandrock, Phys. Status Solidi 16, 487 (1966).
[4]M. Cardona and G. Harbeke, Phys. Rev. 137, A1467 (1965).
[5]J. C. Phillips, J. Phys. Soc. Japan Suppl. 21, 3 (1966).
[6]U. Roessler and M. Lietz, Phys. Status Solidi 17, 597 (1966).
[7]F. Herman and S. Skillman, Atomic Structure Calculations (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1963).
[8]H. Kukimoto et al., Phys. Letters 19, 551 (1965).
[9]Of course, not all of the transitions given in Ref. 4 are necessarily conclusive, but the gap seems to be. The latter is the only experimental value underlying our calculations. A more detailed discussion will be possible when more results are available concerning other II-VI and III-V compounds.
[10]J. C. Phillips, Solid State Phys. 18, 99 (1966).
[11]J. Treusch, Phys. Status Solidi 19, 603 (1967); U. Roessler, Solid State Commun. 5, 45 (1967).

# TWO-MAGNON LIGHT SCATTERING IN ANTIFERROMAGNETIC MnF$_2$

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The strength, line shapes, polarization selection rules, and magnetic field behavior of two-magnon light scattering in antiferromagnetic MnF$_2$ are reported, and they are interpreted in terms of an excited-state exchange coupling between sublattices and the magnon dispersion relation

We present theoretical and further experimental[1] results on the second-order scattering of light by magnons in antiferromagnetic MnF$_2$. The two-magnon spectra are interpreted using the known magnon density of states and a new mechanism for light scattering based on excited-state exchange interactions between the two magnetic sublattices. The theory satisfactorily explains (1) the polarization selection rules governing the scattering, (2) the behavior of the scattering in applied magnetic fields, (3) the relation of the sharp features