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ELECTRONIC STRUCTURE OF THE ANTIFERROMAGNETIC MnTe.

ELECTRONIC STRUCTURE OF THE ANTIFERROMAGNETIC MnTe[x]

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ABSTRACT.

We present band calculation for antiferromagnetic MnTe. MnTe is found to be a semiconductor with indirect energy gap of 0.35 eV. The density of states and reflectivity spectra are presented and compared with experiment. As a result of comparison we conclude that optical properties of MnTe can be described in the framework of band theory.

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1. - INTRODUCTION.

Among transition metal compounds possessing NiAs (D_{6h}^4) crystalografic structure MnTe is particularly interesting example. Most of the material beloning to this group is metalic and MnTe is one of a few semiconductors known. Alike other manganese chalcoge nides MnTe is antiferromagnetic at low temperatures. MnO, α-MnS and MnSe are also insulators, but their stable structure is NaCl and their resistivities are by several orders of magnitude higher than this of MnTe. So, as it has been pointed out already by Allen et al.[1], MnTe is an example of a crossroad material between manganese, halcogenides and metalic transition metal compounds.

During last few years there is a growing interest in the materials called (somewhat controversionally) "semimagnetic semiconductors"[2]. Typically, they are II - VI semi-conducting compounds alloyed with manganese, e. g. $Cd_xMn_{1-x}Te$ or $Hg_xMn_{1-x}Te$, with concentration of manganese going up to as much as 70%. Investigation of these materials is quite a new development of solid state physics, being still in its early stage. One of the keys to understanding of their properties is knowledge of the electronic structure of MnTe. Since many years much effort has been invested in experimental[1, 3-14] and, recently, theoretical[14, 15] works concerning MnTe. In spite of that its electronic properties are far from to be known and understood. Making a choice from sometimes contradictory sta-tements we based our calculation on the following facts : MnTe is an antiferromagnet with magnetic moment of $5\mu_B$[13] and Neel temperature T_N of 323 K[12]. The lattice constants are a = 7.79 A and c = 12.66 A below the T_N[3]. From the optical properties measured by Allen et al.[1] it is clear that below T_N MnTe is semiconducting with direct gap of ~1.3 eV, but relatively high absorption below the edge suggests existance of indirect gap at lower energy. No estimation for this gap exist. There is estimation of it (~ 0.4 eV, from temperature de pendence of resistivity[16]) in the paramagnetic region, but antiferromagnetic ordering can change such a small value substantially. Finally, the core level shifts from X-ray photo-emission spectra of Franzen and Sterner[6] and effective charge calculated by Allen et al.[1] suggest ionic model for binding.

Starting from these data we carried out spin-polarized, non-relativistic APW cal-culation of the electronic band structure of MnTe in the antiferromagnetic phase. We pre-sent some details of calculation and their results as well as density of states and one-elec tron optical spectra. Comparing available experimental data and our results, we discuss validity of previously formulated models of the electronic structure of MnTe.

2. - CALCULATIONS.

MnTe crystal structure is shown on Fig. 1a. It consists of two hexagonal sublattices of Mn^{2+} and Te^{2-} ions. Below the Neel temperature Mn magnetic moments of 5 μ_B order ferromagnetically in the hexagonal planes perpendicular to c axis and antiferromagnetically in the chains along this axis. For nonmagnetic case (i. e. when we disregard the changes of exchange potential from plane to plane) the group of symmetry is D_{6h}^4. Accordingly to Slater's spin-polarized $X\alpha$ method[17] of energy levels calculation for magnetically ordered solids the exchange potential for electrons with given spin direction changes from one plane to another. In the both cases, antiferromagnetic and non magnetic, the unit cell consists of four ions, two of manganese and two of tellurium, but as in the latter case both manganese atoms are equivalent, in the former they are not. This formally changes the symmetry group from D_{6h}^4 to D_{3d}^3 [18].
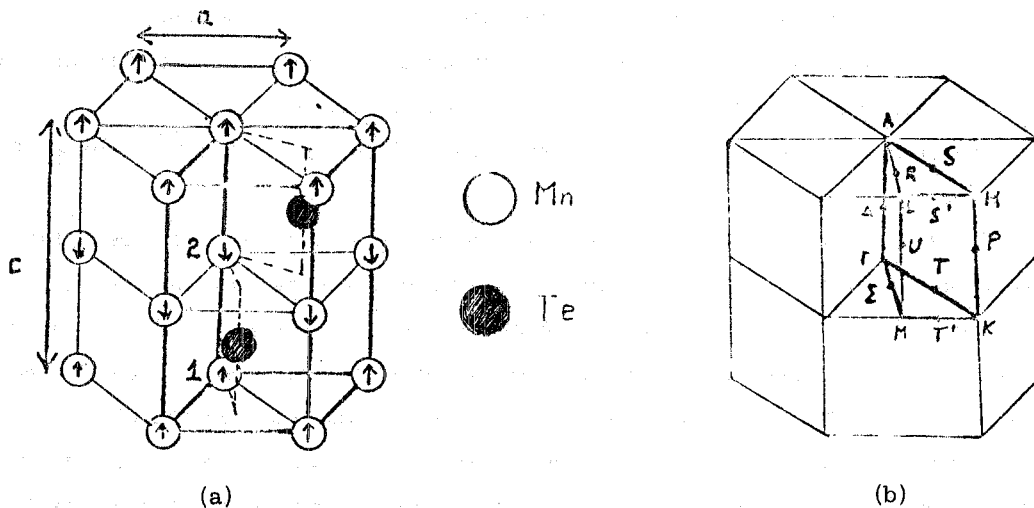

(a)   (b)

FIG. 1 - (a) NiAs (D_{6h}^4) crystalographic structure. Closed circles : Te ions ; open circles : Mn ions ;   (b) Brillouin Zone for NiAs structure and its irreducible part with high-symmetry points.

During construction of crystal potential the Coulomb part of it (and also the exchange part for the Te^{2-}) was calculated from superposition of the total ionic charge densities. For Mn^{2+} exchange potential was calculated separately for electrons with spin "up" and "down" ("up" and "down" should not be understood literally for in the absence of spin-orbit interaction in the calculation direction of magnetic moments with respect to crystal axes is undefin ed) accordingly to

$$V_{ex}^{1\uparrow(\downarrow)}(r) = -6\alpha(3/4\pi)^{1/3}\left[\sum_{\nu}\varrho^{\uparrow(\downarrow)}(r-R_{\nu}) + \sum_{\mu}\varrho^{\downarrow(\uparrow)}(r-R_{\mu})\right]^{1/3}$$

and

$$V_{ex}^{2\uparrow(\downarrow)}(r) = -6\alpha(3/4\pi)^{1/3}\left[\sum_{\mu}\varrho^{\uparrow(\downarrow)}(r-R_{\mu}) + \sum_{\nu}\varrho^{\downarrow(\uparrow)}(r-R_{\nu})\right]^{1/3}$$

where 1 and 2 are Mn^{2+} ions in position 1 and 2 in the unit cell (see Fig. 1a), $\nu(\mu)$ indicates summation over all Mn^{2+} ions in lattice positions equivalent to position 1 (2) and $\varrho^{\uparrow(\downarrow)}$ are Mn^{2+} charge densities of spins "up" and "down". It is easy to note that $V_{ex}^{1\downarrow} = V_{ex}^{2\uparrow}$ and $V_{ex}^{1\uparrow} = V_{ex}^{2\downarrow}$, so, in the antiferromagnetic case, we have to solve for one electronic structure, as opposite to the ferromagnetic case, where we have to find two separate band structures for electrons with spin "up" and "down". In the former case the states of electrons with spin "up" localized on Mn ion located at position 1 are equivalent to states of electrons with spin "down" localized on Mn ion at position 2. The detailed group-theoretical analysis of the problem has been given by Matheiss[18] and Sandratskii[19].

In order to obtain charge and spin density of Mn^{2+} we adopted well-known Liberman's procedure[20] to spin-polarized case. We checked out our results carefully against those of Wilson et al.[21] getting exact agreement. $X\alpha$ exchange potential was used for Mn^{2+} with $\alpha = 0.719$[21] during both atomic and crystal potential calculation.

The charge density for Te^{2-} was generated by Froese-Fischer[22] Hartree-Fock program[x].

Crystal potential was constructed using different α coefficients inside of the muffin-tin spheres for Mn and Te and in the interstitial region. For Mn, the best atomic value was used as we mentioned before and in the interstitial region Gaspar-Kohn-Sham value of $\alpha = 2/3$ was taken. The coefficient for Te was assumed adjustable parameter in order to reproduce the correct value of the direct gap of MnTe. In order to make comparison with very recent work of Sandratskii et al.[15] we performed two set of calculations - with and without warping corrections[23] i. e. with and without taking into account real shape of the potential in the interstitial region. It turned out that influence of the corrections is substantial on account of different sizes of Mn^{2+} and Te^{2-} ions, so we had to adjust Te α coefficient separately for both calculation. The actual values obtained are listed in Table I together with other relevant parameters.

We used unsymmetrized version of APW method with variable basis set[24]. Convergence of ~ 5 mRy has been achieved when hamiltonian size was about 160×160. It is sub-

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(x) This diversity of charge density sources has been caused by troubles we have fallen in when using $X\alpha$ programs for Te^{2-} charge density calculation. Resulting crystal potential led to band structure entirely inconsistent with initial assumptions - we obtained metal-like structure with magnetization equal to zero. It seems that $X\alpha$ procedure should not be recommended for calculation of orbitals of heavy, negative ions. The problem arises from overestimation of exchange by $X\alpha$ potential at long distances, what in turn distorts strongly outer orbitals of the ion.

<div align="center">TABLE I</div>

Atomic configurations:	$Mn^{2+}: 3d^5$, $Te^{2-}: 5s^2 5p^6$
Positions of atoms within unit cell (in Cartesian coordinates):	$Mn^{2+}(1)$ - 0, 0, 0
	$Mn^{2+}(2)$ - 0, 0, c/2
	Te^{2-} - $a/(2\sqrt{3})$, a/2, c/4
	$a/\sqrt{3}$, 0, 3c/4
Lattice constants	a = 7.79 a. u.
	c = 12.66 a. u.
	c/a = 1.625
Muffin-tin radii	R_{mt} = 2.72 (both ions)
α exchange parameters	α_{Mn} = 0.719
	α_{Te} = 0.914 (case a)
	α_{Te} = 0.861 (case b)
	α_{int} = 2/3
Hamiltonian size	150-160 dependently on k-point

stantially less than in the case of other NiAs-type materials[24,25]. Because of the c/a ra tio for MnTe, equal almost exactly to 1.63, the material is as close packed as possible in this structure and this diminishes the APW hamiltonian.

The band energies were calculated at relatively dense mesh of 70 points in the irreducible part of Brillouin Zone (Fig. 1b), 15 of them in the volume of BZ. The dense mesh was used to trace out band profiles beyond any doubts. This is important in the absence of eigenfunctions calculation, when compatibility relations are only source of information on band symmetries. The density of states (DOS) and joint density of states (JDOS) were calculated using improved Gilat-Raubenheimer method[26,27] from Fourier expansion of the bands[26].

3. - RESULTS AND DISCUSSION.

The band structure of antiferromagnetic MnTe is plotted in Fig. 2 along the symmetry lines. The numerical data are given in Table II. Fig. 2a presents the structure calculated with warping correction (case a) and Fig. 2b - without them (case b). In Fig. 3 DOS curves are shown for the both cases. We start with analysis of those dominating features which are common for both calculations. The band diagrams show the complicated sets of 13 valence bands and several conduction bands. Two lowest valence bands are of the Te^{2-} 5s origin. They are separated from p - d 11 bands complex, accomodating 22 MnTe valence electrons.
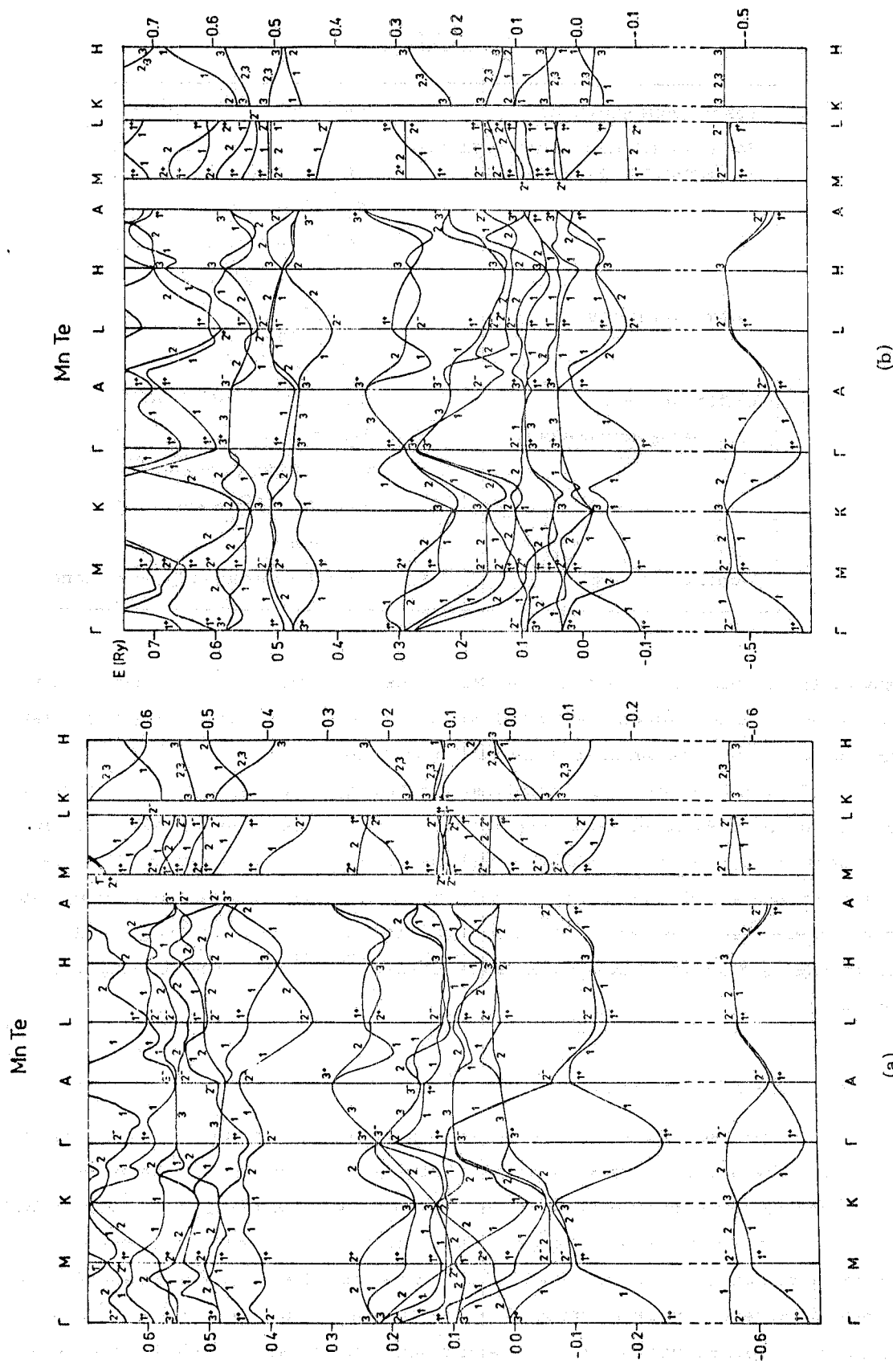
FIG. 2 - The band structure diagrams for antiferromagnetic MnTe. (a) with warping corrections included; (b) without warping corrections.
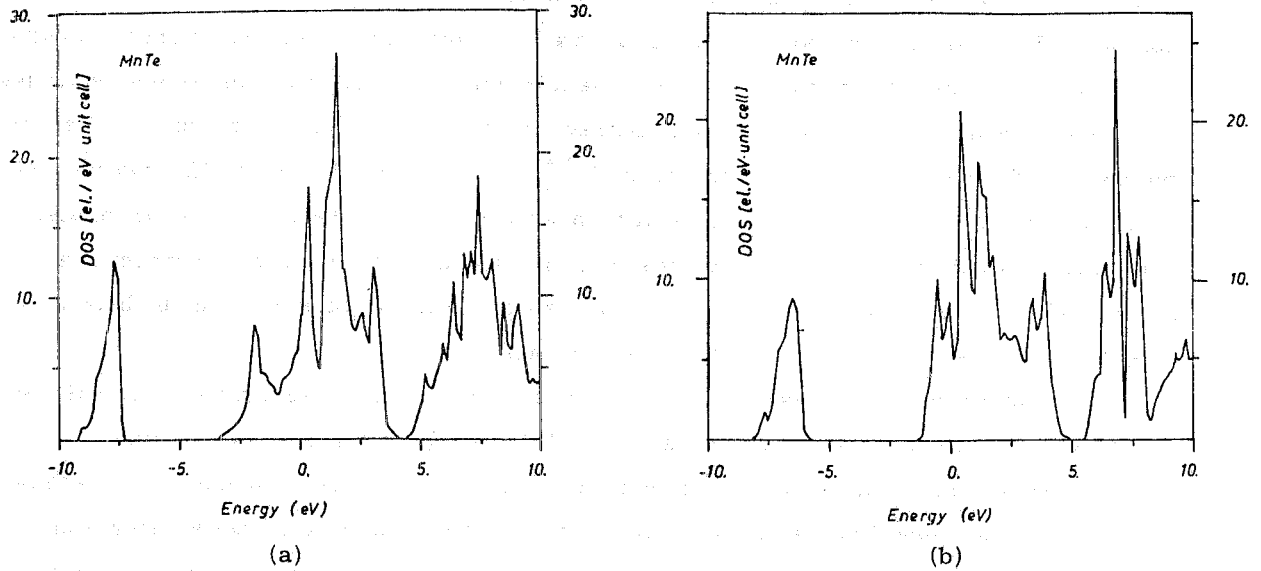
FIG. 3 - The density of states histograms. (a) with warping corrections included; (b) without warping corrections.

TABLE II - Some parameters of the calculated structures.

	case a	case b
Te s-like band width	2. 3	2. 3
Separation between s-band and p-d complex	4. 0	4. 6
p-d complex width	7. 1	6. 1
Mn d "up"-like band width	2. 0	1. 7
Crystal-field splitting of this band	1. 0	0. 8
Distance d-like band onset - top of valence band	2. 1	2. 8
Direct gap	1. 25	1. 3
Indirect gap	0. 35	0. 8
Maximum of valence band	4. 0, A point	4. 7, A point
Minimum of conduction band	4. 35	5. 5

All the entries in electronvolts.

constitued by six Te^{2-} 5p and five Mn^{2+} 3d "up" bands. Although considerable hybridization is unavoidable in such a case, one can clearly see that 3d "up" bands form the center of p-d complex. The maximum of valence band is located at A point and is separated from conduction band by adjusted direct gap of 1. 3 eV. The minimum of conduction band is located in the vicinity of L point, in the volume of BZ. Indirect gap is 0. 8 eV in the case b and 0. 35 eV in the case a. Conduction band is a mixture of Mn^{2+} 4s and 3d "down" states. The main difference between cases a and b is in the relative positions of p-like Te and d-like Mn bands. It is clearly illustrated in DOS histograms (Fig. 3) that inclusion of warping corrections lowers p-like Te bands by roughly as much as 1 eV at the top of valence band and broadens valence band, leaving Mn d-like levels hardly changed.

We interpret two highest peaks in the center of p-d complex as crystal-field splitted d-like levels. Splitting is about 0. 8 eV and 1. 0 eV in the cases b and a, respectively.

More drastic changes occured to conduction band. In the case b it was still possible to distinguish 3d "down" bands at the bottom of conduction band; in the case a conduction band is a mixture of 3d "down" and 4s states of Mn, whole subset being lowered even more than Te 5p states. All these changes are by no means surprising and their physical meaning is obvious. The case b may be compared with recent calculation of Sandratskii et al. [15]. They employed KKR method, in which warping corrections can not be included, starting from atomic rather than ionic configurations and constructing charge density from Clementi's[28] orbitals. The overall agreement of structures is good, especially in the vicinity of energy gap, where even quantitive agreement should be noted. Some discrepancies exist in the structure of the valence band, but qualitative picture is similar if we disregard interpretation of maximum in their DOS curve, 0. 7 eV below the gap. Authors ascribe it to the crystal-field splitted 3d "up" bands and we do not share their opinion. In accordance to our vievw the top of valence band has mainly Te p-like character. Another discrepancy is the value of 3d "up" - 3d "down" splitting. This quantity is almost entirely intra-ionic property of Mn^{2+} ion and should be equal to 0. 44 Ry or 6 eV, independently on compound [17,29]. In APW method this splitting can be estimated from relative positions of logderivative asymptotes for l = 2, calculated from spin "up" and "down" potentials and, as a rule, actual band splitting is equal to this value.

The value obtained in (15) seems to be slightly smaller. It probably follows from the fact that Mn^{2+} magnetic moment was taken equal to 4. 7 μ_B instead of 5 μ_B.

We calculated effective masses at the top of valence band. The masses were calculated directly from APW eigenvalues. Our estimation for $m_\perp$ and $m_\parallel$ are 0. 26 and 0. 32, respectively, as compared to the values of 0. 42 and 0. 66 obtained by Sandratskii. Here agreement is lightly worse and masses calculated by Sandratskii et al. fit better to known experimental data of $m_\perp = 0. 40$ [10] and $m_{av} = (m_\perp^2 m_\parallel)^{1/3} = 0. 53$ [11]. Both of the calculations,

our and that of Sandratskii et al. differ even qualitatively from MnTe$_6$ cluster calculation of de Groot[14]. His calculation has been carried out till selfconsistency. Resulting level's dia gram predicts Te 5s states at the bottom, like in our results, but this is the point where re-semblance comes to the end. 3. 5 eV above Te 5s levels de Groot predicts Mn d "up" levels separated from Te 5p levels by next 3 eV. Mn 3d "up" levels are not splitted by crystal field. The 5p levels have total width of ~ 2 eV and are separated from Mn 3d "down" empty levels by 0. 5 eV. This picture is in clear disagreement with de Groot's phtoemission data. We be-lieve this result can not be a correct one, but reason of such a discrepancy is unknown.

Comparison of our results with experimental data shows, in general, reasonable agreement. Total p-d manifold bandwidth can be estimated from X-ray[6] and UV[14] photo-emission to be around 7 eV, in accordance with value calculated. The spectra in both cases are symmetric, so we can expect that d-like bands with high DOS are located centrally in the p-d manifold. We have also available data of Allen et al.[1] and reflectivity spectra measured by Kendelewicz[5]. The position of the absorption edge found in (1) was used to adjust Te α exchange parameter and therefore agreement is bound to be good. The value of indirect edge is more interesting. Absorption curve in (1) suggest that it should be positioned at very low energies, perhaps below 0. 2 eV. Estimation made in (16) for the paramagnetic region can not be taken seriously because antiferromagnetic order is able to change the bands around the gap substantially[*]. The value of 0. 35 eV obtained by us in the case a seems to be still to high.

The value of crystal-field splitting of Mn^{2+} 3d levels in MnTe is unknown, but the va lue found here is comparable with this of 10100 cm^{-1}, determined experimentally for MnO by Huffman and coworkers[30].

In order to compare our results with reflectivity spectra we calculated one-electron optical functions, i. e. JDOS(ω), $\varepsilon_2(\omega)$ and then, using Kramers-Kronig transformation, $\varepsilon_1(\omega)$, and R(ω). ε_2 was calculated using constant matrix element approximation and only direct transitions were taken into account i. e. $\varepsilon_2(\omega)$ was equal to zero for $\hbar\omega < E_g^{direct}$. Our conduction bands were calculated only up to the energy of ~ 7 eV above the energy gap, therefore for $\hbar\omega > 8$ eV, $\varepsilon_2(\omega)$ was replaced in Kramers-Kronig formulae by tail function of the form $\varepsilon_2 = \beta\omega/(\gamma^2 + \omega^2)^2$ with $\gamma = 4. 5$ eV[31]. We normalized $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ and R(ω)

(*) It should be noted, however, that suggestion of Sandratskii et al.[15] that without magnetic ordering (ferro- or antiferromagnetic) MnTe would be a metal with high value of DOS at the Fermi level is entirely incorrect. Mn^{2+} 3d "up" and "down" states splitting is an in-traionic effect and has nothing to do with ordering of moments in solid. The true statement is that paramagnetic state of materials in which magnetic moments persist above Neel or Curie temperatures can not be handled properly within a framework of band theory, as every disordered system.

spectra equalizing $\varepsilon_1(0)$ to the value of $\varepsilon_\infty = 11.4$ found by Allen et al.[1].

One must realize that all this procedure yields rather crude estimation of $R(\omega)$ spectrum. Constant matrix element approximation and neglect of indirect transition, especially below E_g, can change sugnificantly intensities of maxima in resulting spectra, although we do not expect drastic changes in maxima positions. The main shortcoming is that we are calculating absorption from ground state of the system. For Bloch electrons Koopmans theorem[36] provides a basis for such a procedure. In the case of MnTe we are dealing with mixed system of Bloch and localized electrons and, therefore, we might expect that optical spectrum will be a complex combination of band-like transitions and localized excitations which should be described in the framework of ligand-field theory. It has been proved in numerous works[32] that optical and photoemission spectra of manganese and other transition metal oxides can be successfully interpreted in terms of localized excitations. On the other hand, optical properties of metalic transition metal compounds having D_{6h}^4 structure can be described accurately in the framework of band theory[24,33].

In such a situation we found it interesting to compare experimental reflectivity spectrum with that calculated, in which direct interband transition is only mechanism of absorption. The results are shown in Fig. 4, compared with experimental curve measured by Kendelewicz[5]. This is only result we were be able to trace out in literature. Allen and coworkers[1] also measured reflectivity spectra in visible and close UV but the log-log plot present
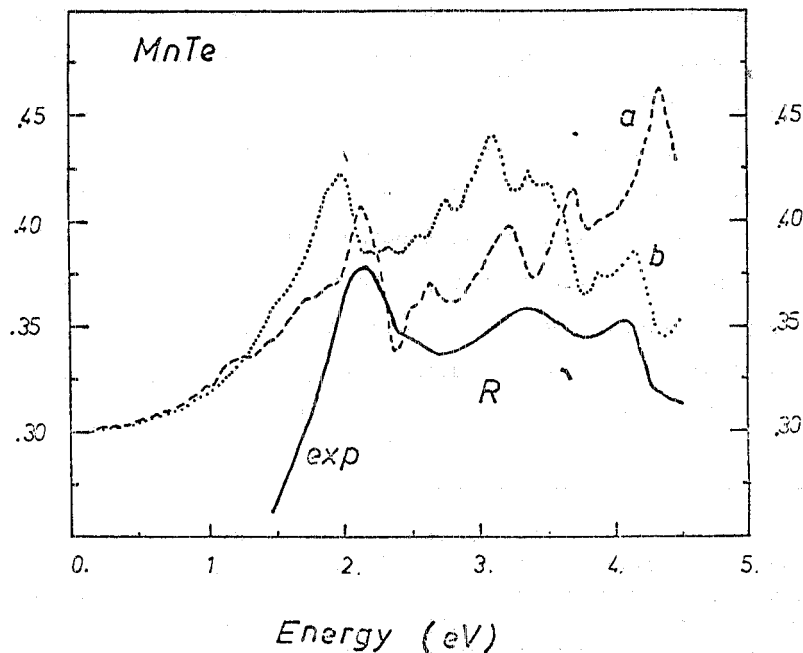

FIG. 4 - Reflectivity coefficients of MnTe. Only direct transitions were included. Dotted line: case b, dashed line: case a, solid line: experimental curve from (5).

ed in their work does not enable us to make any quantitative comparison. Kendelewicz[5] presented a number of spectra. Their shape varies significantly from sample to sample. We choose the spectrum recomended by author as the most reliable one.

It would not be honest to say that agreement is astonishing, for it is not, nor in the case a neither in the case b, but for the reasons already enumarated we did not expect good agreement and what we obtained fits better to experiment than we hoped it will. The positions of three main maxima are reproduced with accuracy of 0.2 eV. Our conclusion is that up to energy of 4.5 eV it is not necessary to recall localized transitions in order to interprete optical spectra of MnTe. We did not trace out detaily the bands and regions of the Brillouin Zone giving main raise to the observed maxima, but it is sure that in energy range up to ~4 eV the contribution of 3d "up"-like electrons is negligible on the account of depth they are sunk into p-like bands manifold.

We observe, of course, transitions to 3d "down"-like bands but their delocalization is significant and they can be treated as Bloch electrons.

What we have said above does not exclude possibility of the existence of localized excitation. Nevertheless, their observation can be very difficult. Transition of this type are doubly unallowed (change of spin and multiplicity), thus their intensities are small and it would be not easy to find them of the strong background produced by band absorption.

Kendelewicz[5] interpreted two higher maxima in $R(\omega)$ spectrum as localized transitions of the type $3d^5 - 3d^4(^5E) + 4s$ and $3d^5 - 3d^4(^5T_2) + 4s$. We do not see any need for such an interpretation for the reasons mentioned before. Beside, we estimated energy for such transitions for Mn^{2+} ion, using Slater's[34] formulae and Mann's[35] integrals. The lowest limit we found was well above 4.8 eV, so we exclude interpretation proposed by Kendelewicz.

In order to summarize, we cocnlude that our band structure confirms qualitative model proposed by Allen and coworkers (Fig. 1c in (1)), except the structure of conduction band where 3d "down"- and 4s-like bands of Mn^{2+} are mixed by far stronger. Mn^{2+} 3d "up" band is dived into Te^{2-} manifold much deeper than it was expected. As a result of that the optical properties of MnTe can be described in the framework of band theory rather than ligand field theory.

The underestimation of the value of 3d bands spin splitting is main shortcoming also of the Allen's model for MnO, MnS and MnSe (Fig. 1a in (1)). We can not accept such a crude picture in which the band theory approach is totally mixed with that of ligand field. Allen and coworkers argue that according to the $X\alpha$ method of finding spin-polarized band structures the Frenkel exciton $3d^5$ multiplet structure observed in the absorption spectra has approximately the energy of the spin splitting of 3d bands. This is rather poor approximation even if we consider the average energy of multiplets, and putting the energy of the lowest multiplet onto one-electron energy diagram is even more risky idea.

As we mentionad, the spin splitting of 3d bands in manganese is about 6 eV (rather high value in comparison to 2.1 eV which is energy of the lowest multiplet) and we understand · 3d "down" levels in isolated ion as virtual states with zero occupancy. In the ion, the value of spin splitting does not correspond to the value of any real excitation - multiplets theory must be employed in order to get description of excited states. In a crystal these levels are signifi cantly delocalized, but their average energy does not change much. On account of Koopman's theorem[36] we can observe optical transitions to these states and this is exactly situation we have in MnTe. We believe that for MnO and other Mn halcogenides this mechanism will give contribution to absorption at energies higher than separation between p-like bands of chalco gen and 3d "down"-like bands of manganese. This mechanism can not be understood if one relays on Allen's band diagram. In order to improve it Mn 3d "down" bands should be pushed up into the conduction band by approximately 4 eV. If it is necessary to put many-electron ex citations onto one-electron energy diagram, the method adopted by Messick et al.[32] seems to be much better.

ACKNOWLEDGMENTS.

REFERENCES.

(1) - J. W. Allen, G. Luckowsky and J. C. Mikkelsen, J. Sol. Stat. Comm. 24, 367 (1977).
(2) - See, for example, R. R. Gałazka, 14th Intern. Conf. Phys. Semicond. , Edinburgh 1978 (1979), pp. 133-140.
(3) - S. Onàri, T. Arai and K. Kudo, Sol. Stat. Comm. 14, 507 (1974).
(4) - K. Ozawa, S. Anzai and Y. Hamaguchi, Phys. Letters 20, 132 (1966).
(5) - T. Kendelewicz, Ph. D. Thesis, Warsaw University (1979), unpublished.
(6) - H. Franzen and C. Sterner, J. Sol. Stat. Chem. 25, 227 (1978).
(7) - T. Hulliger, in "Structure and Bonding" (1968), Vol. 4, p. 190.
(8) - L. V. Povstyanyi, V. I. Kutho and A. S. Zviagin, Sov. Phys. Sol. Stat. 14, 1346 (1972)
(9) - K. Sugihara, J. Phys. and Chem. Solids (GB) 34, 1727 (1973).
(10) - G. Zanmarchi, J. Phys. Chem. Solids 28, 2133 (1967); G. Zanmarchi and C. Haas, Phillips Res. Rep. 23, 389 (1968).
(11) - J. D. Wasscher, Phillips Res. Rep. 24, Suppl. 8, 1 (1969).
(12) - J. J. Banewicz, R. F. Heidelberg and A. H. Luxem, J. Phys. Chem. 65, 615 (1961).
(13) - E. Uchida, H. Kondoh and N. Fukuoka, J. Phys. Soc. Japan 11, 27 (1956).
(14) - R. A. de Groot, Ph. D. Thesis, Univ. Of Groeningen (1976), unpublished.
(15) - L. M. Sandratskii, R. F. Egorow and A. A. Berdyshev, Phys. Stat. Sol. (b) 104, 103 (1981).
(16) - A. I. Zviagin, L. V. Povstyanyi and P. M. Arefieva, Izv. Akad. Nauk SSSR, Ser. Fiz. 35, 1190 (1971).
(17) - J. C. Slater, in "Self-consistent Field for Molecules and Solids" (McGraw-Hill, 1974), Chap. 3 and 11.
(18) - L. F. Matheiss, Phys. Rev. B10, 995 (1974).
(19) - L. M. Sandratskii, Izv. Vuzov. Fiz. (Tomsk) 9, 20 (1979).
(20) - D. Liberman, J. T. Waber and D. T. Cromer, Phys. Rev. 137, A27 (1965).
(21) - T. M. Wilson, J. H. Wood and J. C. Slater, Phys. Rev. A2, 620 (1970).
(22) - Ch. Froese-Fischer, Can. J. Phys. 41, 1895 (1963).
(23) - P. D. De Ciccio, Phys. Rev. 153, 931 (1967).
(24) - H. W. Myron and F. M. Mueller, Phys. Rev. B17, 1828 (1977).
(25) - M. Podgòrny and C. Wijers, Sol. Stat. Comm. 34, 233 (1980).
(26) - G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966); L. J. Raubenheimer and G. Gilat, Phys. Rev. 157, 586 (1967).
(27) - M. Podgòrny and C. Wijers, to be published.
(28) - E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables 14, 220 (1974).
(29) - T. M. Wilson, Int. J. Quantum Chem. 3S, 757 (1970).
(30) - D. R. Huffman, R. L. Wild and M. Shinmei, J. Chem. Phys. 50, 4092 (1969).
(31) - J. P. Walter and M. L. Cohen, Phys. Rev. 183, 764 (1969).
(32) - See, for example, L. Messick, W. C. Walker and R. Glosser, Phys. Rev. B6, 3941 (1972); D. E. Eastman and J. L. Freouf, Phys. Rev. Letters 34, 395 (1975).
(33) - C. Wijers, R. Smetsers, A. R. de Vroomen and M. Podgòrny, J. Phys. F, to be published.
(34) - J. C. Slater, Phys. Rev. 165, 655 (1968).
(35) - J. B. Mann, Los Alamos Sci. Rep. LA-3690 (1967), unpublished.
(36) - T. C. Koopmans, Physica 1, 104 (1933).