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SUMMARY PAPER AT PARIS CONFERENCE ON IV-VI COMPOUNDS, JULY 1968

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Résumé. — Nous passons ici en revue l'état présent de la question dans différents domaines de la recherche sur les composés IV-VI en soulignant particulièrement les problèmes à résoudre.

Abstract. — A review is given of the present status of several of the main areas of investigation of the IV-VI compounds, with the emphasis placed on problems that still have to be solved.

It would be presumptuous of me to give a critique of all of the diverse things that have been discussed at this conference, since we have covered quite a lot of ground. I shall simply try to point out some things that I regard as new progress or residual problems, obviously biasing my remarks towards those parts of the subject with which I feel most at ease.

Crystal Structure and Perfection. — First, let me make a few remarks about crystal structure and perfection. Much of the crystal structure is very well established. However, it is to be noted that, when one is evaluating measurements on epitaxial thin films, one has to be careful about the degree of strain and the mechanism of strain release. We have had some experience in my laboratory of taking a thin PbS film deposited on a backing — a very good epitaxial layer — and subjecting it to a cycle of high hydrostatic pressure, when it was established quite unambiguously that we were producing first considerable uniaxial elastic strain and eventually plastic flow in the film as a result of the difference in compressibility between film and substrate. This is consistent with the expectation that epitaxial films deposited at high temperatures and then cooled may be considerably strained because of the difference in thermal expansion coefficient between film and substrate. Dr. Zemel referred to this possibility and to the deduction that in his work there was found to be zero strain in his films at room temperature. Of course this does not mean that no strain is present at other temperatures, so that a mild warning about the possibility of strained films and about uncritical comparisons of film and bulk data would seem to be appropriate.

A remaining problem in this category would seem to be the establishment of the phase diagram between

SnTe and GeTe. The original work suggested a phase transition, cubic to rhombohedral, in the SnTe near 0 °K. However, this deduction emerged from extrapolations from work on GeTe-SnTe alloys, and careful reexamination suggests rather that the phase transition could occur anywhere between 0 °K and 80 °K. I think it is quite important for the proper interpretation of all of the low temperature data that the question of distortions away from cubic structure be resolved. In fact it is important for the interpretation of the band structure calculations that we have accurate data on lattice constants and on distortions in all of the parent materials and their alloys.

One final remark in this category. It might be interesting for those engaged in the deposition of epitaxial films to try to deposit GeTe in the cubic phase by using a cubic substrate, or alternatively to attempt to put down SnTe in the rhombohedral phase by using, say, the rhombohedral GeTe as substrate. Measurements of the reflectivity of the cubic GeTe could then be compared with those on the normal rhombohedral variety to provide evidence on the differences in electronic band structure produced by the slight distortion from the cubic symmetry.

Band Structure. — First, a trivial point. In some of the early papers — those of Pratt and his collaborators at M. I. T., and those of Kleinman and his collaborators — there was a difference in the symmetry of the lowest conduction band state in PbTe. Specifically, Kleinman and Lin found that the conduction band of PbTe was derived from the L_3 state in the single group notation, whereas the conduction bands of PbS and PbSe were derived from a L_2 state. Actually, it appears that these states are so mixed by spin-orbit interaction that this is somewhat of an

academic question, and the conduction band state is L_6^- in all three crystals. Nevertheless, it is probably worth remarking that this ambiguity about the parentage of the L_6^- conduction band does exist in the literature.

Now let me make a few remarks about relativistic corrections. I think, after the attention which has been paid to such terms in the Hamiltonian over the last two or three years, that everyone accepts that a calculation not taking account of them will very likely give incorrect results. There is some question, however, about the emphasis we should place on these terms in the Hamiltonian when we are extrapolating to new band structures or interpolating band structures for alloys. It seems to me that in recent publications undue emphasis has been placed on this part of the Hamiltonian relative to other parts and I propose to illustrate this thesis with an example.

TABLE I

Substance	Energy Gap ($L_6^+ - L_6^-$)	Lattice Constant A^0	$\Delta(L_6^+(v) - L_6^-(c))$ vol
PbTe	~ 0.2 eV	6.42	—
SnTe	~ -0.3 eV	6.31	~ -0.15 eV
GeTe	~ -0.2 eV	5.99	~ -0.6 eV

In table I, I have set down for PbTe, SnTe and GeTe their lattice constants, and the change in the energetic separation of $L_6^+(v)$ and $L_6^-(c)$ caused by the change in volume *alone*, using the PbTe value as starting point. I have used approximate values for the difference in deformation potential of these states culled from the experimental work of Dr. Prakash in my laboratory on the three lead salts. These are the changes in band gap you would get by ignoring any change in the constituent atoms, and so in the electrostatic potential or in the relativistic corrections, and simply took account of the change in volume. In the case of SnTe, the volume correction has nearly closed the gap to zero by itself, while in GeTe, whose actual band gap is about 0.2 eV, a compensating correction to the volume one is required. I am not suggesting that the volume corrections are the most important ones; I do suggest that the identification of the relativistic shift as the cause of inversion may over-emphasize its importance. When there are several contributing physical mechanisms it may make sense from an historical point of view to say that the inclusion of such and such an overlooked term corrected the situation; it does not make sense to emphasize it to the exclusion of other contributions when extrapolations to other substances or alloys are made. Thus the extrapolation PbTe \rightarrow SnTe \rightarrow GeTe has to

be carefully done including all changes in the Hamiltonian. Another case which has come up at the Conference is that of PbTe-CdTe alloys, where the band gap *increases* even though a cation giving a smaller relativistic correction to the energy of the valence band maximum is being added.

While I am on the subject of band structure, I should like to remark on what I consider reasonably well established and what may not be established in these compounds. The L-symmetry of the conduction and valence band extrema in the lead compounds is pretty well established. The temperature coefficients of their fundamental energy gaps are positive, while those of the fundamental gaps of SnTe and GeTe are negative. Dr. Howard (*) has suggested that the matrix elements of the momentum between the conduction and valence band extremum states of SnTe and GeTe are equal, and he has suggested also that there is a lighter mass second valence band in SnTe and a heavier mass second valence band in GeTe. Dr. Andreev, on the contrary, wants to see heavier second valence bands in both SnTe and GeTe.

I think we would all probably agree that the L_6^+ state is very sensitive to pressure, temperature, or anything else we do to it. It is the valence band maximum state in the lead compounds and its behaviour is largely responsible for the sign of the temperature coefficient of the fundamental gap. From the opposite sign of the gap temperature coefficient in SnTe and GeTe we guess that the L_6^+ state is probably not the valence band maximum state in either SnTe or GeTe. That however does not force it to be the conduction band minimum state in these compounds, as it has been postulated to be. Let me act the devil's advocate for the moment. You can take the L_6^+ state out of the situation by sending it deeper into the valence band instead of turning it into a conduction band. For the moment, we forget about relativistic corrections to the energy of S-like states, and simply demand that the L_6^+ state no longer be the maximum of the valence band. Then we have a situation where we might be able to fit the temperature dependence of the gaps in SnTe and GeTe from the displacements of states other than the L_6^+ . Of course I know there are arguments suggesting that the conduction band in SnTe and GeTe has L_6^+ symmetry; I have described a very different possibility to emphasize that, whereas the identification of the L_6^+ state as the valence band

(*) The substance of Dr Howard's remarks, which will not form part of the Conference Proceedings, is to be found in an article by Tsu, Howard and Esaki, *Phys. Rev.*, 172, 779 (1968).

maximum in the lead compounds is soundly based on Knight shift measurements, we do not have an equally credible identification of the postulated L_6^+ conduction band in the tin compounds. (No n -type SnTe !) It might be a good idea if we could figure out some experiments giving information on the symmetry of the states in the tin and germanium compounds, and especially the symmetry of the SnTe conduction band.

Temperature Coefficients of Gaps and Masses. — Now I'd like to make some comments on the temperature dependence of energy gaps. You will recall that the opposite sign of coefficient between PbTe and SnTe is quoted as one argument for the inversion of the band structure between these compounds. It seems worthwhile reviewing qualitatively the several reasons for temperature coefficients. The first usually quoted is a change in volume caused by the thermal expansion. From the results of pressure experiments we recognize that this contribution may be positive or nega-

tive. The second reason offered is a change in the electron-phonon interaction. The theory for this, first given by Fan and by Radkowsky, leads to a displacement of the absolute extremum of a band into the forbidden gap and an increase in the effective mass. It is conceivable, but somewhat unlikely, that interaction with other bands could alter this qualitative result. Band edges which are not absolute extrema may shift either way with temperature, since some interactions perturb their energy to greater values, and some to lesser. Thus, this second contribution, the explicit electron-phonon interaction, is expected to lead to a decrease in the fundamental energy gap.

I shall describe the experimental situation in a little more detail than is usual. Table II shows experimental results for PbS, PbSe and PbTe, obtained by Dr. Prakash in my laboratory. The experimental T -coefficients of the gaps for PbS, PbSe and PbTe are $+ 5 \times 10^{-4}$ eV/°K, $+ 4.1 \times 10^{-4}$ eV/°K and $+ 4.5 \times 10^{-4}$ eV/°K. These are average values taken from the displacement

TABLE II

	PbS	PbSe	PbTe
Experimental $\left(\frac{dE_g}{dT}\right)_P :$	$+ 5 \times 10^{-4}$ eV/°K	$+ 4.1 \times 10^{-4}$ eV/°K	$+ 4.5 \times 10^{-4}$ eV/°K
Experimental $\left(\frac{\partial E_g}{\partial P}\right)_T :$	$- 9.15 \times 10^{-4}$ eV/bar	$- 9.1 \times 10^{-4}$ eV/bar	$- 7.4 \times 10^{-6}$ eV/bar
$- 3\left(\frac{\alpha}{K}\right)\left(\frac{\partial E_g}{\partial P}\right)_T :$	$+ 2.95 \times 10^{-4}$ eV/°K	$+ 2.45 \times 10^{-4}$ eV/°K	$+ 1.7 \times 10^{-4}$ eV/°K
$\left(\frac{\partial E_g}{\partial T}\right)_V :$	$+ 2.05 \times 10^{-4}$ eV/°K	$+ 1.65 \times 10^{-4}$ eV/°K	$+ 2.8 \times 10^{-4}$ eV/°K

of absorption edges, which change shape slightly with temperature. The pressure coefficients are

$$- 9.15 \times 10^{-6} \text{ eV/bar, } - 9.1 \times 10^{-6} \text{ eV/bar}$$

and $- 7.4 \times 10^{-6}$ eV/bar. The effect of thermal expansion is then given by $- 3(\alpha/K) (\partial E_g/\partial P)_T$ where α is the linear coefficient of thermal expansion and K is the compressibility. The pressure coefficients are thus converted to implicit temperature coefficients of the gaps of $+ 2.95 \times 10^{-4}$ eV/°K, $+ 2.45 \times 10^{-4}$ eV/°K and $+ 1.7 \times 10^{-4}$ eV/°K, leaving explicit contributions $(\partial E_g/\partial T)_V$, which are all positive. This fact, which has been known for some time, means that the theory for the explicit effect in the literature — the only published one — is inadequate for the lead salts.

Now, several years ago Brooks and Yu at Harvard

worked out a different theory of the temperature dependence of band edges and band gaps which has not yet been published. This theory suggests that one obtains a lower order correction (than the self energy correction of Fan) to the energy of an electronic state by computing the energy at finite temperature as an average over all configurations of the lattice ions. The electronic energy is conveniently expressed in terms of the pseudopotential Fourier coefficients Professor Cohen described, and the computation reduces to evaluation of the changes in these coefficients with temperature. Brooks and Yu found that each Fourier coefficient $V(q)$ of the pseudopotential was proportional to $e^{-W(T)}$, i. e., to the square root of the Debye-Waller factor. Different Debye-Waller factors have to be applied to the components of the pseudo-poten-

tial derived from different atoms in the crystal, since they vibrate with different amplitudes. Thus, depending on the symmetry of the wave function about one atom or another, you can get bigger or smaller corrections to the $V(q)$, and this implies positive or negative corrections to specified energy separations. The theory needs to be made more quantitative. One has to be careful that the pseudopotential coefficients are being properly scaled for change in lattice constant as well as a statistical average being taken for the harmonic part of the vibration. These however are the details : the important thing is that gap decreases are possible in principle using this theory. Such a theory validates the contentions of Dimmock et al. regarding the use of the T dependence of the gap to specify band symmetries. Note again that the Fan theory did not do this. Perhaps we should coin a new term to describe the displacement of a band edge with temperature : I suggest « temperature deformation potential » by analogy to volume deformation potential and strain deformation potential.

Similar remarks apply to the temperature dependence of effective masses. The effect of the electron-phonon interaction on the mass is usually deduced to be an increase. Yet it must be noted that Dr. Ravich concludes that the fractional changes of mass and energy gap with temperature are equal under assumptions valid for the lead salts, both for the pure volume effect and the explicit electron-phonon interaction effect. In Dr. Ravich's theory the virtual scattering of a conduction band electron to all of the conduction and valence band states throughout the Brillouin zone is taken into account and this, it is asserted, can give both the quoted relation and an increase of gap with temperature. Offhand, I don't understand a proof of this in absence of an established band structure throughout the zone and a k -dependent scattering matrix element. The theory pays no heed to the Brooks-Yu mechanism.

The theory of the explicit temperature dependence of masses badly needs more definitive work. It is to be noted that the use of formulae from k - p theory at finite temperature is not admissible until they are underpinned by some theory such as that of Brooks-Yu or Ravich. It is also to be noted that it has been established experimentally that the Ravich relation quoted above does not hold in the case of GaAs. It could well be that the Brooks-Yu correction is especially important for lattices such as PbTe with dissimilar atoms and atomic vibrations, and when one is considering states predominantly S -like around one of the two atoms. For other lattices, and less S -like

states, the self energy corrections may be relatively more important. This however is pure speculation and the problem is one of the major unsolved ones.

A brief remark on systematics : the size of the fundamental gap in PbSe is out of order from the atomic progression PbS, PbSe and PbTe. However, this seems to be the only physical parameter that is out of progression and is presumably the result of some accidental cancellation.

Zero Gaps. — A brief remark also on the occurrence of zero gaps in certain alloys. The experimental evidence is that in alloys of lead and tin chalcogenides the fundamental energy gap decreases as a function of composition to some minimum value (which may be zero) and then increases again. Although one often sees references to decreases of the gap to zero, there are reasons to believe that the gap may never become exactly zero, and that in fact crystalline distortions may occur that maintain a tiny gap. This interesting possibility should be watched by those decreasing the gap to small values in alloying and pressure experiments.

Second Valence Band. — The second valence band has been referred to often at this conference. There would seem now to be authoritative evidence for the presence of two such bands in all of the lead compounds from experiments on the abrupt changes of density-of-states mass and of susceptibility mass with composition, from the high temperature optical experiments where the temperature coefficient of the gap changes, and from the adjustment of interband energy separation by hydrostatic pressure. The details, however, are still very much in question. The most violent disagreement is between the requirement of Howard of a second band in SnTe of lighter mass and that of Andreev of just the opposite. It seems to me to be entirely possible that Dr. Howard's suggestion of three bands participating differently in the different experiments being analyzed is correct, and it is notable that this is not in disagreement with the conclusions of the band calculations. It suggests that alloying, stress or doping experiments should be done that will emphasize one type of mass or the other. There are other troublesome points about these valence bands. According to Zemel (quoting Brebrick) the gap in $\text{Pb}_x\text{Ge}_{1-x}\text{Te}$ alloys does not pass through zero. If this implies that the band state ordering in PbTe and GeTe is the same (not a unique deduction) then it is inconsistent with the fact that the fundamental gap of GeTe, like of SnTe, decreases with rise in temperature, while that of PbTe increases. This observation

of Brebrick's, please note, is unexpected if we rely on extrapolation from the change in relativistic corrections to the energy of the L_6^+ state as we replace Pb by Ge.

Scattering. — It was clear to me from the papers on scattering that such analyses must be as sophisticated as is humanly possible if we are to have any hope of obtaining credible values of the parameters involved. Apparently one must take account simultaneously of non parabolic bands, non ellipsoidal energy surfaces, and scattering by acoustic and optical modes and by the impurities, all affected by the complication of considerable electron-electron scattering.

Devices. — Dr. Melngailis has given us an up-to-date report on progress on devices at Lincoln Laboratory. It is clear that the lifetime for radiative recombination is short, but it is not yet clear how important are other intrinsic recombination processes such as Auger effect and multiphonon emission. These latter effects would be expected to become increasingly important as the fundamental energy gap is reduced in lead-tin telluride alloys. The influence of natural defects is always present but one would hope to be able to get rid of these to some extent. In the area of small gaps, produced either by alloying, or pressure, or both, there is rich promise not only for laser, photovoltaic or photoconductive devices, but also for fundamental physical studies of the interaction of electrons with lattice vibrations. The pressure measurements are particularly appealing since they appear to change the fewest parameters and probably do not affect the density of lattice defects as do alteration of temperature or alloy content.

Superconductivity. — Now a few remarks on the last paper on superconductivity. The question of whether distortion is a significant parameter for the observation of superconductivity in the IV-VI compounds has not been mentioned. Yet, in a situation where the physical mechanisms are not wholly understood, correlations of parameters may be instructive, and it does appear that we have superconductivity in GeTe and SnTe accompanied certainly by distortion in the case of GeTe and possibly in SnTe, whereas in the lead compounds we find neither distortions nor superconductivity. Another point not discussed this time by Professor Cohen was the possibility of the necessity for population of the second valence band in order for there to be a superconducting transition. In a sense the effect of the second valence band was buried in Professor Cohen's parameter for the interband deformation potential.

One may also ask why we have superconductivity in SnTe and not in PbTe. One obvious difference between them is the difference in the top of the valence band, which implies that their interband deformation potentials are also different. The question of the influence of the second valence band should be investigated experimentally by shifting it relative to the first, say by pressure, uniaxial stress, alloying or doping. For example, the addition of PbTe to SnTe leads to a decrease in fundamental gap and band edge effective mass, which means that the filling of the uppermost valence band is altered. Barring accidental cancellations, one might expect to observe shifts in the transition temperature from which clues as to the mechanism of the superconductivity might be inferred.

Optical Properties. — The shape of the fundamental absorption edge was not discussed at this conference. In the lead compounds the absorption coefficient varies as $\alpha = A \exp[(h\nu - E_g)/E_0]$ below the edge, and as $\alpha = B(h\nu - E_g)^{1/2}$ just above it. The parameter E_0 is temperature dependent. I suppose this means that some of the older estimates of gaps carried out by fitting absorption curves differently should be treated with caution. The photoluminescence also shows an exponential tail. Clearly theoretical work is needed on this Urbach rule type of behaviour. Prakash has suggested that the random E-fields due to the LO lattice vibration are large enough to cause the tail.

Dr. Seraphin has reported on the reflectivity and electroreflectivity at energies high above the fundamental edge. His caution in interpreting these data to give information about the band structure seemed very well justified to me who has followed from the beginning the sequence of unjustified deductions, retractions, etc., which have characterized this sort of analysis. It is clear that this type of measurement, carried out as a function of doping, may help to identify any transition which begins or ends near the Fermi Level. Unfortunately, there is also the possibility that the electron-hole interaction will also alter the structure of transitions between energy states far from the Fermi level. One could also conceive of repeating the electroreflectivity as a function of uniaxial stress in order to obtain the k -vector of the states involved in transitions.

These, then, are a few remarks on questions raised by the subject matter of the conference. I have not had the time to give a complete review and no doubt in some areas such as lattice vibrations or ferroelectricity there remain vital questions which have gone completely unremarked.

DISCUSSION

STRAUSS A. J. — We have obtained preliminary data by means of differential thermal analysis which appear to confirm the existence of a phase transition in SnTe in the vicinity of 70-75 °K.

The fact that superconductivity has not been observed on PbTe may be due to the unavailability of data for samples containing more than 10^{20} cm^{-3} . Experiments on more highly doped samples, prepared by the technique of Andreev would appear to be desirable.
