UCRL - 76894
PREPRINT
Conf-751116--11

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November 18, 1975

This paper was prepared for submission to
the IEEE 1975 Nuclear Science Symposium
San Francisco, CA, November 19-21, 1975

THEORETICAL BAND STRUCTURE ANALYSIS ON POSSIBLE HIGH-Z DETECTOR MATERIALS*

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Abstract

Theoretical energy band structure calculations have been utilized to investigate several high-Z materials for potential use as ambient temperature radiation detectors. Using the pseudopotential technique, the band structure for HgI_2 has been determined and the effective masses of the holes and electrons have been estimated. Theoretical mobilities of the electrons and holes as a function of temperature have been computed for HgI_2 and CdTe and are compared to experimental data.

Introduction

In the search for semiconductor crystals suitable for ambient temperature radiation detection, basic criteria such as high-Z, appropriate energy band gap, and a sufficiently high mobility-lifetime ($\mu\tau$) product are necessary. In many of the high-Z compounds that appear to be of interest, information concerning the $\mu\tau$ product for holes and electrons and the magnitude and type of band gap structure is lacking. As a result, this information has to be generally obtained by experimental means using single crystals.

An accurate determination of band gap character and $\mu\tau$ product generally requires a relatively perfect single crystal. The initial evaluation of high-Z materials as possible detectors, then, usually involves a comprehensive crystal growth program which includes a study on the control of extrinsic and intrinsic nonstoichiometry during growth. A research program of this type is usually expensive and time consuming. It is therefore desirable to establish a research technique for initially investigating and evaluating compounds of interest without the initial step of growing high purity, stoichiometric single crystals.

A research approach based on theoretical band structure analysis can provide the necessary information concerning the ability of high-Z materials to meet the basic detector requirements. By applying this analysis to selected compounds of interest, it is possible to determine whether the crystal has a direct or indirect band gap, the magnitude of the bandgap, and the hole and electron effective mass. From the effective mass values, the hole and electron mobility of these compounds can then be calculated. The data obtained by this method can be used to decide which high-Z compounds are worth pursuing a concentrated effort for single crystal growth.

Selection of High-Z Compounds

In a complete investigation of possible ambient temperature detector materials, it is necessary to examine the high-Z elements of the Periodic Table. Selected elements of a high-Z nature are indicated in the Periodic Table shown in Figure 1. The elements are designated as either a cation or anion depending upon their behavior in compound formation. Most binary compound semiconductors of potential interest on the basis of high Z would involve the anions Te, I, and amphoteric Sb. Because of the fact that few binary tellurides, iodides, or antimonides can meet the band gap requirement, the anion group has been extended to include Se and S. The elements, O and Br, are not included since the oxides and bromides generally have a highly ionic character because of the large electronegativity difference between the cation and anion.[1] This implies that these materials have high band gaps and low mobilities.[2,3] The inclusion of S is mainly due to the fact that it has the same electronegativity value as I and therefore some of the sulfides would have an ionicity similar to their iodides. As a result, sulfides may be of interest due to their ability to adjust the band gap in the investigation of ternaries even if their binary compounds are not useful.

The high-Z materials that have been thus far used as ambient temperature radiation detectors are basically CdTe and HgI_2. However, both materials have inherent inadequacies in that the $\mu\tau$ products tend to be too small for high resolution detector applications. Utilizing the technique of band structure analysis, we are currently searching for other high-Z materials which would be useful as γ-ray detectors at room temperature. As a means of checking the exactness of the band structure analysis technique in accurately describing the potential suitability of a material, the analysis has been initially applied in confirming the experimental data for CdTe and HgI_2.

Theoretical Energy Band Computation

Perhaps the most powerful method used today for energy band calculations is the pseudopotential technique. In this method, the potential energy of the electron is expressed in the following form:[4,5]

$$V_{ps}(\vec{r}) = \sum_{G} V_{ps}(G) e^{i\vec{G} \cdot \vec{r}} \qquad (1)$$

where the constants $V_{ps}(G)$ are determined from the condition that the energy levels at certain points in the Brillouin Zone agree with that obtained experimentally. The summation in equation (1) is over all the reciprocal vectors pertaining to the solid. For most of the crystals that have been studied so far[6] this series has been found to converge very rapidly; hence, only a few constants are needed for evaluation. Once the constants have been determined, the resulting pseudopotential is used to calculate the energy band structure for the whole Brillouin Zone.

In searching for new materials as possible high energy photon detectors, almost all of the materials that look promising have been found to have insufficient data for computing their pseudopotential. It was found

*This work was performed under the auspices of the U.S. Energy Research and Development Administration under contract number W-7504-ENG-48.

that either the experimental data does not exist or that the data is too inconsistent to allow determination of the pseudopotential constants. However, by using transferability properties of the pseudopotential technique,[5] one can obtain an approximate pseudopotential. In the determination of the pseudopotential for materials having inadequate data, the transferability of the pseudopotential technique is utilized.

Band Structure Analysis

As a first attempt in studying the band structure analysis approach for investigating high-Z materials, an energy band calculation was made for HgI_2. The calculation was made using an approximate pseudopotential obtained by the transferability of pseudopotentials. The pseudopotential of Mercury was taken from the work of Brandt and Rayne[6] and is shown in Figure 2. For Iodine, the result of Schluter and Schluter[7] showed that the pseudopotential can be written:

$$V_i(\vec{G}) = \frac{\left[A_1(G^2 - A_2)\right]}{\left[e^{A_3(G^2 - A_2)} + 1\right]} \qquad (2)$$

where $A_1 = 6.5$ $\qquad A_3 = 0.46$

$A_2 = 1.6$ $\qquad A_4 = -6.5$

The numerical values of the constants for Iodine have been slightly changed to bring the calculated energy band gap of HgI_2 in agreement with experimental data.

The Brillouin Zone of HgI_2, showing some symmetry points, is given in Figure 3. Using the pseudopotentials of Mercury and Iodine, the energy band structure of HgI_2 was calculated for all symmetry directions. The smallest energy gap was found to occur in the Γ - M direction of [110]. In this direction, the bottom of the conduction band does not occur at the same point in k-space as that of the top of the valence band. This implies an indirect band gap transition. In addition the second and third valence bands are found to be degenerate, regardless of symmetry direction.

The present work indicates that the conduction band is s-like, in contrast with the energy band structure of PbI_2 in which the conduction band is p-like.[8] The s-like nature of the conduction band seems to confirm the experimental results of Kanzaki and Imai.[8] The fact that the bottom of the conduction band and the top of the valence band do not occur in the same k-space confirms the experimental findings of Chester and Coleman.[9] This interpretation is still only tentative. Calculations including the spin-orbit interaction and careful symmetry considerations are needed to determine the exact shape of the conduction and valence bands. Contour plots for the bands are also needed in order to confirm whether they are s-like or p-like in character.

Theoretical Mobility Computation

Carrier mobilities are one of the more important parameters that must be known in predicting the potential use of a material for detector applications. This parameter, in turn, depends on the hole and electron effective masses. From the band structure calculations, it is possible to determine an estimate of the effective mass of the charge carriers by taking the second derivative at the bottom of the conduction band and at the top of the valence band. To obtain a more accurate value for the effective mass, it is necessary to take into account the spin-orbit interaction, especially in the case of high-Z materials. However, as a reasonably accurate first order approximation, the hole and electron effective masses were calculated from the second derivative without spin-orbit considerations. To demonstrate that the pseudopotential technique does indeed give reasonable accuracy in the determination of the effective mass, the technique was applied to several II-VI compounds. Using existing pseudopotentials,[5] the electron effective mass was calculated and compared with experimental data[10] as shown in Table I. It is seen that the calculated effective mass and experimental values agree quite well - within 20 percent.

In general, there are different types of phonons in a solid which can interact with holes and electrons. These different types include the acoustical phonons, the optical phonons, and the polar optical phonons. In the case of an ionic crystal, the most important interaction is the polar optical phonon interaction. For a layered structure crystal, however, both the optical and the polar optical phonons are important.[11,12]

There are numerous ways that can be used to derive the hole and electron mobility for a crystal where the optical phonons are considered to be dominant.[12-15] In the present paper we will use the following:[13]

$$\mu = \bar{\mu} F \qquad (3)$$

where

$$\bar{\mu} = \frac{3\gamma(kt)^{3/2}}{2^{7/2}\pi^{1/2} q m^{3/2}} \frac{e^z - 1}{e^{z/2}} \qquad (4)$$

$$F = \left\{ \left(z^6 + \frac{37}{4} z^4 + \frac{165}{4} z^2 + \frac{217}{8} \right) K_1^2 - \left(2z^5 + \frac{19}{4} z^3 + \frac{1081}{32} z \right) K_1 K_0 - \left(z^6 + \frac{23}{4} z^4 + \frac{299}{8} z^2 \right) K_0^2 \right\} \Big/ \left\{ \left(\frac{35}{4} z^4 + \frac{75}{2} z^2 + 24 \right) K_1^3 + \left(\frac{3}{2} z^5 + \frac{85}{8} z^3 - 18z \right) K_1^2 K_0 - \left(\frac{47}{4} z^4 + \frac{117}{2} z^2 \right) K_1 K_0^2 - \left(\frac{3}{2} z^5 + \frac{183}{8} z^3 \right) K_0^3 \right\} \qquad (5)$$

and

$\hbar\omega$ = polar optical phonon energy

m = effective mass of either electron or hole

$z = \frac{\hbar\omega}{kT}$

$\frac{1}{\gamma} = \frac{\omega^2}{4\pi} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)$

K_0, K_1 = zero and first order Bessel Functions.

Using equation (3) along with the parameters given in Table II, a theoretical mobility curve was obtained for CdTe. A comparison of the theoretical and the experimental mobility[17,18] for the electrons and holes as a function of temperature is shown in Figures 5 and 6, respectively. The effective mass used for the mobility of holes (m_h = .43 m_o) was that calculated by the pseudopotential technique. The agreement with theory and experimental results are excellent, especially for the hole mobility curve.

In the case of HgI_2, the crystal is a layer structure and the bonding forces between atoms are different for different crystalline directions. The interaction between atoms in the c-direction is mostly due to van der Waals forces while the bonding of atoms in the a-direction is mostly covalent. Fivaz and Mooser have derived expressions for mobility in layered structures.[12] According to their work, the mobility in a layered structure for an optical phonon interaction can be written:

$$\mu_{yy} = \frac{e\hbar}{2m_x\hbar\omega}\ \frac{1}{4\pi g^2}\left(\frac{e^{\hbar\omega/kT}-1}{1+\frac{\hbar\omega}{2kT}}\right) \qquad (6)$$

and

$$\mu_{zz} = \mu_{xx}\ \frac{12I_z^2(2m_x d_z^2)}{kT\pi^2\hbar^2}\left(1+\frac{\hbar\omega}{2kT}\right) \qquad (7)$$

where g is defined as the coupling constant between the electron and the optical phonon, m_x is the effective mass in the direction perpendicular to the c-axis, d_z is the effective distance between the layers, $\hbar\omega$ is the optical phonon energy, and I_z is the overlapping energy.

Equation (6) and (7) are based upon a simple layer structure model. As a result, it is not expected that these equations can exactly predict the mobility of a complicated layer structure such as HgI_2. In addition, there are many unknown parameters associated with equations (6) and (7). Consequently, only a tentative judgment concerning any agreement or disagreement can be made in the comparison of experimental data of HgI_2 and the results of equations (6) and (7).

Since the energy of the optical phonon is not known for this crystal, it was assumed that its value was the same as the polar optical phonon energy which is about 0.013 eV.[8] The coupling constant g is approximately 0.25.[12] The overlapping energy integral I_z was estimated to be of the order of 0.01 eV using:

$$I_z \approx \left(\frac{\hbar}{d_z}\right)^2\ \frac{1}{2m_{h_{11}}} \qquad (8)$$

The effective mass for the electron and hole were estimated from the energy band calculation to be:

$$m_e \cong 0.4\ m_o$$

$$m_h \cong 1.2\ m_o$$

$$m_{h_{11}} \cong 3.5\ m_o$$

Because there was good agreement between the theory and the experimentally determined effective mass for the II-VI compounds, it is assumed that the above values for HgI_2 are a good approximation to the true effective masses.

Based upon the assumption of the value of the optical phonon energy and the approximation made for the constant I_z, the theoretical mobility of the holes and electrons was calculated. A comparison of experimental data[17] with the theoretical mobility due to both polar optical scattering and optical scattering is shown in Figure 7 for holes and in Figure 8 for electrons.

Discussion and Summary

The intention of this paper was to discuss a theoretical method to select potential high-Z detector materials. The approach is principally based on the concept of electronegativity differences of elements as it applies to the degree of ionic bonding. Although the degree of ionicity of a compound can be loosely related either directly or indirectly to the band gap and mobility, it does not provide sufficient information. The phenomenological approach cannot give detailed information as to whether the band gap is direct or indirect. In addition, it cannot provide the necessary data for determining effective mass so that calculations of mobility as a function of temperature can be made. Consequently, the pseudopotential technique was used to supplement the phenomenological approach in obtaining the energy band structure of a crystal. From the band structure it is possible to determine, to a first approximation, the type of energy gap transition. Also, it is possible to estimate the hole and electron effective mass and provide an estimate of the mobility for the charge carriers. To show the accuracy of the pseudopotential approach, electron effective masses were calculated for several II-VI compounds. The theoretical results agree well with experimental values.

In the present paper, preliminary results for the band structure of HgI_2 have been presented. The effective masses of the holes and the electrons have been estimated. Using these values, the theoretical mobility of the charge carriers have been calculated as a function of temperature. It has been shown that the agreement of theoretical and experimental results are very good for holes.

It is of interest to conjecture as to which scattering mechanism controls the behavior of the electron mobility with temperature in HgI_2. If optical phonon scattering is more important that polar phonon scattering, then, from equations (6) and (7), the mobility in the c-direction should have a very different temperature dependence than the a-direction. This is not the case as shown in Figure 8. Experimental data of Figure 8 further indicates that the electron mobility is almost independent of crystalline direction. Based upon the fact that the reflectivity is almost isotropic and that the conduction band is s-like, one would expect that the dielectric constant and the conduction band effective mass should also be somewhat independent of direction. Consequently, comparison of theory an experimental evidence implies that polar phonon-electron interaction is the most important scattering mechanism in HgI_2.

In calculating the theoretical mobility for the electrons and the holes in HgI_2, the existing reflec-

tivity data was used to estimate the dielectric constants for this crystal.[8] In applying equation (4) to HgI_2, the anisotropic nature of the crystal was neglected. The neglect of anisotropy was justified based on the fact that the reflectivity data is quite isotropic when the excitation wavelength is away from the fundamental absorption edge.[8] This assumption has also been made for crystals such as GaSe.[13]

The band structure analysis approach is presently being applied to the investigation of other interesting high-Z materials of binary and ternary composition.

Acknowledgements

The technical assistance of G. Myers for his programmatic help is gratefully acknowledged.

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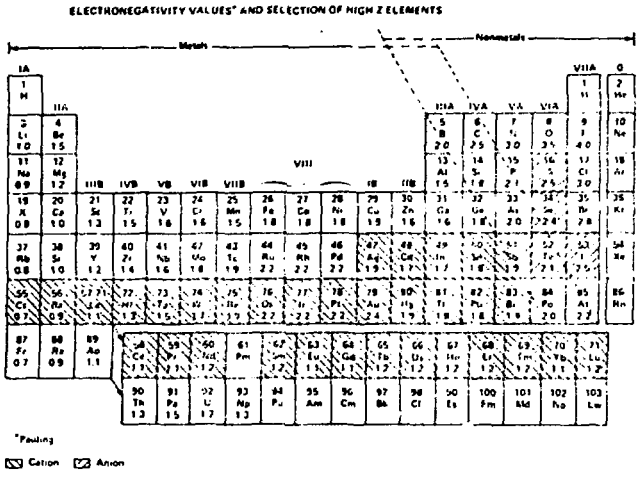

Figure 1. Selected elements for the investigation of possible ambient temperature detector compounds.

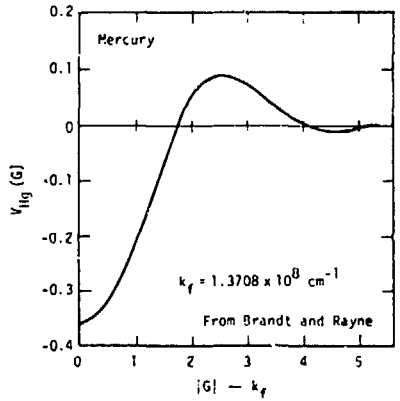

Figure 2. Pseudopotential of Mercury

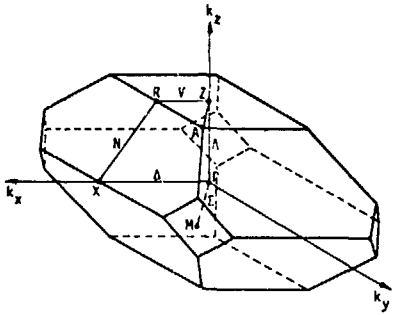

Figure 3. The Brillouin Zone of HgI_2 with some symmetry points indicated.

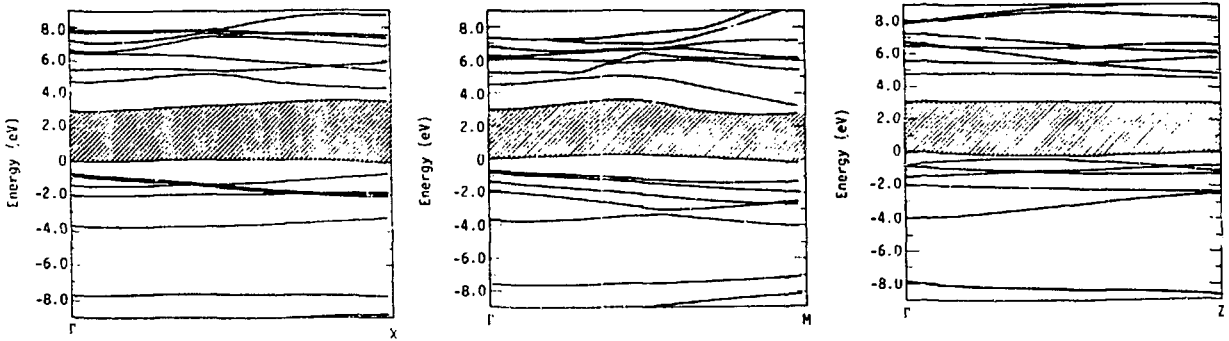

Figure 4. Energy band structure of HgI_2 for three symmetry directions.

TABLE I

Effective mass of some II - VI compounds

Compound	Electron m*	
	Theory	Experimental [a]
Cd Te	0.15	0.14 ± 0.02
Zn S	0.21	0.24
Zn Se	0.173	0.13 - 0.17
Zn Te	0.16	0.20

[a] Reference 10

TABLE II

Physical parameters of Cd Te

Parameter	Value [b]
m_e/m_o	0.0963
ϵ_o	9.6
ϵ_∞	7.13
$\hbar\omega$	0.021 eV
q*	0.5 q

*Effective charge

[b] Reference 16

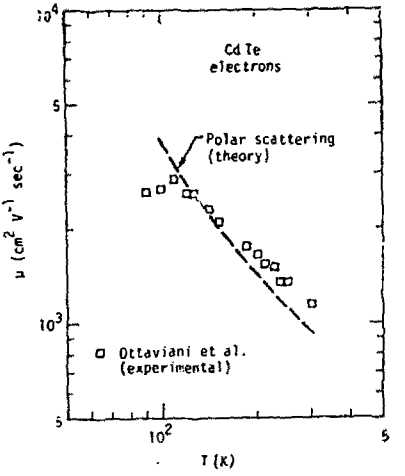

Figure 5. Mobility of electrons in CdTe as a function of temperature. A comparison of the theoretical mobility due to polar optical phonon scattering is made to experimental data [17]

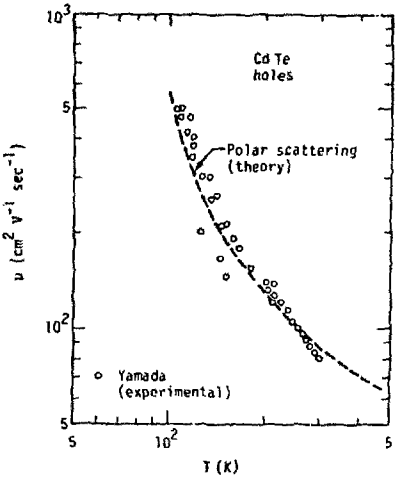

Figure 6. Hole mobility of CdTe as a function of temperature. Experimental data [18] is compared to the theoretical mobility due to polar optical phonon scattering.

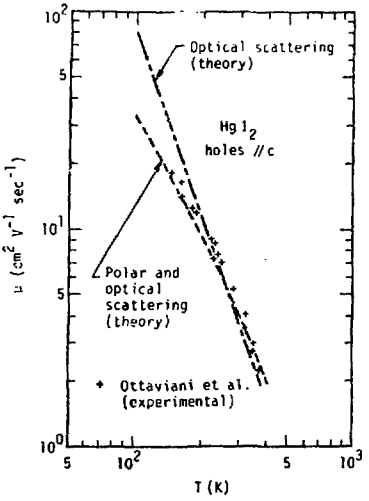

Figure 7. Mobility of holes as a function of temperature parallel to the c-axis of HgI_2. Theoretical mobility due to optical phonon scattering only and scattering due to both polar and optical phonons are compared to experimental data.[17]

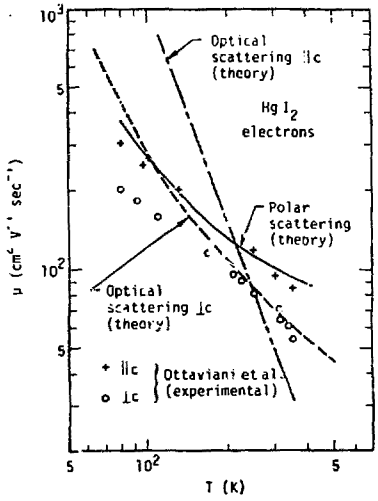

Figure 8. Mobility of electrons as a function of temperature parallel and perpendicular to the c-axis of HgI_2. A comparison of the experimental data[17] to the theoretical mobility due to different phonon scattering mechanisms is shown.