

Returnable Electron-Phonon Interaction in the II-VI Compound AlloysE. M. Sheregii,¹ J. Cebulskii,¹ A. Marcelli,² and M. Piccinini²¹*University of Rzeszów, Rejtana 16c, Rzeszów 35-959, Poland*²*INFN - Laboratori Nazionali Frascati,
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In this paper is shown that the singularity in the energy band-structure which is the zero-gap state in the HgCdTe or ZnHgTe alloys, causes a discontinuity in the temperature dependence of the transverse optical phonon frequency at temperatures at which it occurs.

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I. INTRODUCTION

It is well known that the electron-phonon (e - p) interaction is the main mechanism of the charge-carrier scattering in semiconductor crystals and low-dimensional structures, as well as scattering in impurities and defects. In particular, the scattering on the long wave longitudinal optical ($\text{LO}(\Gamma)$) phonons has a universal character because the last one generates the macroscopic polarized pole, and electrons interact very effectively with the pole. There are several resonance effects that cause a change in the electron energy spectrum via interaction with $\text{LO}(\Gamma)$ phonons. These effects are caused by direct e - p interaction (influence of the phonons on the electron energetic spectrum) and have been described in review articles and books [2, 3]. The role of the effects caused by direct nonlinear e - p interaction was shown in Ref. [4]. On the other hand, the effects caused by returnable electron-phonon interaction, i.e., the influence of electrons on the phonon spectrum, are not as well understood. Recently, in our previous study [5], it was shown that the singularity in the electron energy spectrum results in the discontinuity of the temperature dependence of the phonon frequency in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys. The reverse e - p coupling that produces this resonance effect has a non-polarized character; however, a deformation mechanism exists.

It is interesting to extend the study of this effect to an investigation of the effect on other semiconductor compounds. Simultaneously, an important problem associated with the temperature dependences of the HgTe-like phonon modes can be solved by carrying out these investigations. It was shown earlier [6] that the temperature shift of the HgTe-like TO-phonon frequency is opposite to the normal characteristics of the temperature shift of the phonon frequency for alkali compounds as well as for most semiconductor compounds; in particular, the frequency increases when the temperature increases. In contrast, the normal temperature shift caused by the crystal lattice dilatation (a consequence of anharmonicity) is of the opposite nature: the frequency decreases when the temperature increases. This contrasting behavior was explained qualitatively in Ref. [6]: the e - p interaction produces

positive frequency shifts as the temperature increases, and the magnitude of these shifts exceeds that of the negative shifts because of anharmonicity.

The rich experimental data on the reflectivity in the far infrared region of the $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys, as obtained in the DAFNE-light facility in Frascati between 2002 and 2006 for different compositions and a wide range of temperatures by using synchrotron radiation as an effective source, present a unique opportunity for carrying out a quantitative examination of this hypothesis.

II. THEORY

As mentioned above, a deformation of the potential that is responsible for the interaction of electrons with TO-phonons is believed to be the predominant mechanism of returnable e - p interaction, because only the TO-phonons are clearly recognized in the optical reflectivity experiments.

Following Gontmacher and Levinson (Ref. [3]), the e - p coupling constant $V_{n,n'}(k, q, s)$ for the TO-phonons with a small wave vector q is

$$V_{n,n'}(k, q, s) = \left(\frac{\hbar}{2MN\omega_{TO}} \right)^{\frac{1}{2}} \frac{1}{a} \Xi_{n,n'}(k, q) e(q, s), \quad (1)$$

where n and n' are the Bloch states, and s is the index of the phonon modes. $\Xi(k, q)$ is the matrix that represents the optical deformation potential, and it is given by the following formula:

$$\Xi_{n,n'}(k, q) = a \int \psi_{n',k+q} \frac{\partial V}{\partial u} \psi_{n,k} dr, \quad (2)$$

where $\Psi_{n,n'}(k)$ is the Bloch function with the wave vector k for the n -th band, V is the crystal potential, N is the number of unit cells per unit volume, $e(q, s)$ is the phonon polarization vector, u is the relative displacement, M is the reduced mass of two different ions (in the case of III-V and II-VI compounds, the ions are the cation and anion dipole pair), and a is the lattice constant.

We are interested in only those elements of the deformation potential matrix that correspond to the region between the valence and the conduction band. Therefore, as in Ref. [7], the self energy of the TO-phonons with a small wave-vector q is given by the formula

$$\omega_{TO}^{*2} = \omega_{TO}^2 - \int dE F(E) \left\{ \frac{1}{E + E_g + \hbar\omega_{TO}} + \frac{1}{E + E_g - \hbar\omega_{TO}} \right\}, \quad (3)$$

where E_g is the energy gap and

$$F(E) = \frac{2}{(2\pi)^3} \int \frac{\omega_{TO}}{\hbar} |V_{cv}(k, q)|^2 \cdot \delta(E - E_c(k+q) - E_v(k)) dk. \quad (4)$$

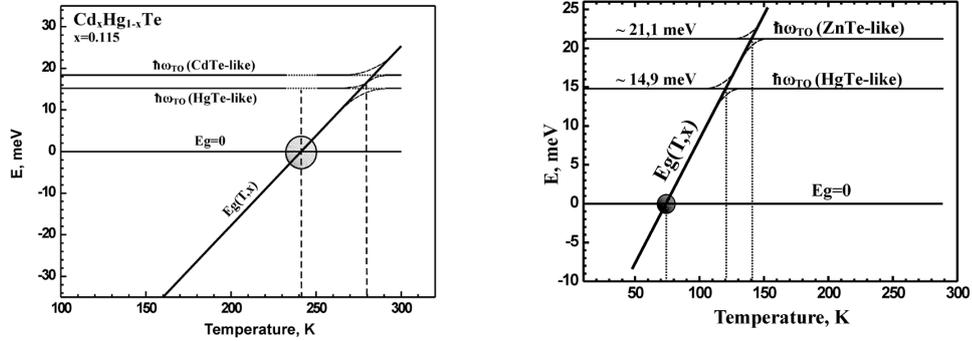


FIG. 1: The temperature dependence of $E_g(T)$ for the solid solutions: (a) $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x = 0.115$) and (b) $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.06$).

$V_{cv}(k, q)$ in equation (4) does not depend on the wave vector of the long-wave optical phonons ($q \approx 0$); thus, $E_c(k + q) - E_v(k) = E_g$.

We can identify two kinds of singularities in equation (3): the first kind of singularity is obtained when E_g is equal to $\hbar\omega_{TO}$, and the second is obtained when E_g equals zero. In the first case, the splitting of the optical phonon frequency dependence $\omega_{TO}(T)$ occurs when the electron-phonon interaction couples two electron states (Γ_6 and Γ_8) such that some “pinning” effects appear at $\hbar\omega_{TO} = E_g$ because of the anti-crossing of two interacting states. A significantly different effect is expected for the dependence $\omega_{TO}(T)$ in the second case, i.e., at the temperature at which $E_g(T) = 0$. If the temperature increases, the $E_g(T)$ dependence approaches zero from the negative side of the energy gap (the inversion band-structure). On the other hand, if the temperature decreases, the $E_g(T)$ dependence approaches zero from the positive side of the energy gap (normal band structure). Hence, a discontinuity in $\omega_{TO}(T)$ could occur at $E_g(T) = 0$, whereas, according to Ref. [7], only a softening of the phonon optical modes occurs as the frequency decreases.

In Figs. 1(a) and 1(b), the temperature dependence of E_g for the solid solution $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x = 0.115$) and $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.06$) has been calculated using the empirical formulas for $E_g(T, x)$ [8] that were experimentally verified to be accurate [9]. In Fig. 1(a), we also plot the ω_{TO} -phonon frequency corresponding to the HgTe- and CdTe-like modes as well as HgTe- and ZnTe-like modes for such HgCdTe and HgZnTe [11] compositions. It should be emphasized that the condition $E_g = 0$ occurs at 245 K and 85 K for $\text{Hg}_{0.885}\text{Cd}_{0.115}\text{Te}$ and $\text{Hg}_{0.94}\text{Zn}_{0.06}\text{Te}$, respectively.

III. EXPERIMENT

In order to investigate the temperature behavior of the phonon modes for the HgZnTe and HgCdTe alloys, a cycle of experimental measurements of optical reflectivity in the far-

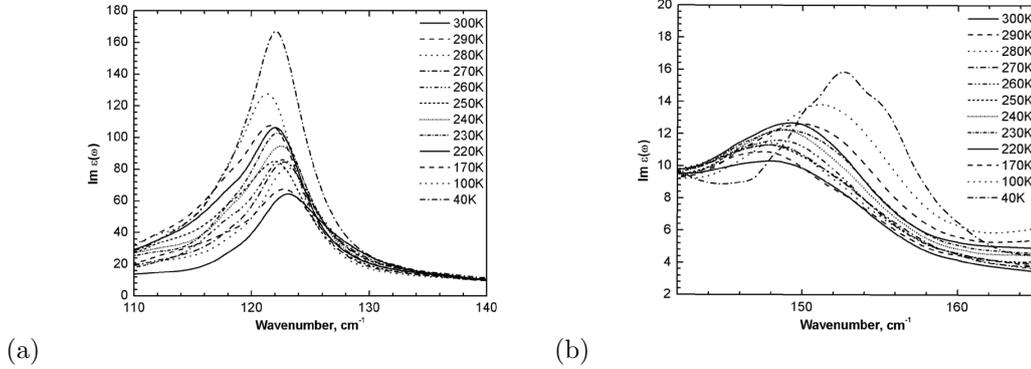


FIG. 2: Imaginary part of the dielectric function $\text{Im}[\varepsilon(\omega, T)]$, as calculated from reflectivity spectra of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x = 0.115$) samples (Fig. 2) by using the Kramers-Kronig transformation in the region $110\text{--}140\text{ cm}^{-1}$ (a) and in the region $142\text{--}165\text{ cm}^{-1}$ (b).

infrared region were performed from 2002 to 2006. Some of the measurements were carried out at the DAFNE-light laboratory at Frascati (Italy) using synchrotron radiation as the source (the experimental setup is described in Ref. [10]). The Bruker Equinox 55 FT-IR interferometer that was modified in order to measure spectra in vacuum was employed. The synchrotron radiation from the DAFNE storage ring and a mercury lamp were used as IR sources. Measurements were performed at temperatures ranging from 20 to 300 K and at wavenumbers ranging from 50 to 600 cm^{-1} ; the measurements are described in detail in Ref. [5]. Note that the reflectivity coefficient $R(\omega, T)$ was measured with an accuracy of about 0.2%. The spectral resolution was 1 cm^{-1} in a majority of the cases, and it was 2 cm^{-1} in some cases.

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals were grown at the Institute of Physics, Polish Academy of Sciences, Warsaw (Poland), and $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ crystals were grown at CNRS, Groupe d'Etude de la Matière Condensée, Meudon (France).

We calculated the imaginary part of the dielectric function from the reflectivity spectra by adopting the Kramers-Kronig (KK) procedure. The imaginary part was calculated with an estimated uncertainty of approximately 1.5% for all experimental data. The results are shown in Figs. 2(a) and 2(b), where, for $\text{Hg}_{0.885}\text{Cd}_{0.115}\text{Te}$, $\text{Im}[\varepsilon(\omega, T)]$ for the HgTe-like mode (a) is compared with that for the CdTe-like mode (b) at different temperatures in the interval 30 K–300 K. Here, we emphasize that the maximum of the HgTe-like sub-band is shifted toward lower frequencies when the temperature increases from 30 K to 240 K, while for temperatures higher than 245 K, the maximum shifts to higher frequencies. At 245 K, there is a discontinuity in the temperature dependence for the HgTe-like mode. Slight non-monotonicity in the temperature dependence of the CdTe-like sub-band maximum frequency position near 245 K is observed. The frequencies at which the maxima of the $\text{Im}[\varepsilon(\omega, T)]$ curves at different temperatures between 30 K and 300 K are observed in the HgTe-like and ZnTe-like sub-bands were investigated in the case of the $\text{Hg}_{0.80}\text{Zn}_{0.20}\text{Te}$

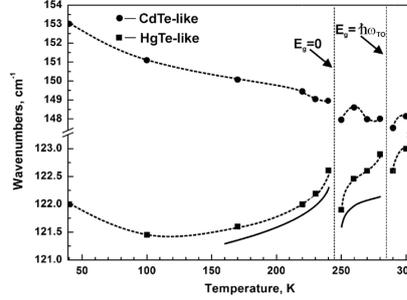


FIG. 3: Plot of the frequencies in terms of the wavenumber against temperature for the HgTe-like (T_0 -mode) and CdTe-like (T_1 -mode) sub-band maxima on the $\text{Im}[\varepsilon(\omega, T)]$ curves (Fig. 2 a,b). The solid curves are calculated using equation (5) (further details in text).

sample as well.

The frequencies at which maxima of the $\text{Im}[\varepsilon(\omega, T)]$ curves are observed at different temperatures between 40 K and 300 K in the HgTe-like and CdTe-like sub-bands for the $\text{Hg}_{0.885}\text{Cd}_{0.115}\text{Te}$ sample are shown in Fig. 3; the same frequencies for the HgTe-like and ZnTe-like sub-bands are shown in Fig. 4.

IV. DISCUSSION

The crystalline structures of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ were characterized by the presence of tetrahedra, each of which has a central ion surrounded in the first coordination shell by four nearest neighbors (NN) at the vertices. In the $A_xB_{1-x}Z$ ternary tetrahedron structures, different tetrahedron configurations T_n (n : number of B-atoms in the tetrahedron) coexist; two of these are strictly binary structures corresponding to the AZ and the BZ compounds, whose lattices are characterized by the tetrahedron units T_0 and T_4 (configurations), respectively, and three are strictly ternary structures characterized by the configurations T_1 , T_2 , and T_3 . In an ideal crystal lattice, they generate a total of at least $(2 \times 1) + (3 \times 2) = 2 + 6 = 8$ optically active phonon modes. These are canonical phonon modes (CPMs) [12], some of which, as mentioned above, appear as a fine structure of the two bands in the ranges $118\text{--}135\text{ cm}^{-1}$ and $140\text{--}160\text{ cm}^{-1}$ for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, as shown in Figs. 2(a) and 2(b), and in the ranges $118\text{--}135\text{ cm}^{-1}$ and $160\text{--}180\text{ cm}^{-1}$ for $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$.

In this study, when $x = 0.115$ or 0.06 , the T_0 component is predominant in the crystal lattice. The corresponding mode in the HgTe-like sub-band is the strongest mode, and it determines the maximum of this sub-band. For the CdTe and ZnTe-like sub-bands, the Cd-Te as well as Zn-Te oscillations in the T_1 -tetrahedra generate the maximum. Therefore, as shown in Figs. 3 and 4, the frequencies at which maxima occur in the sub-bands are those corresponding to these two modes (generated by tetrahedra T_0 and T_1) at different

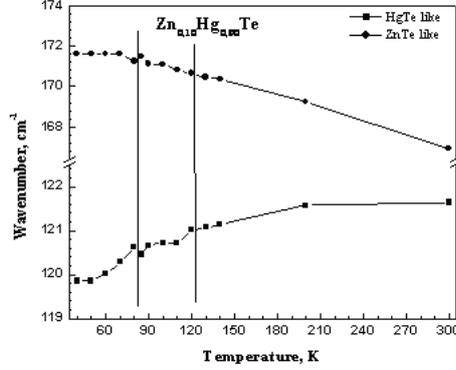


FIG. 4: Plot of the frequencies in terms of the wavenumbers against temperature for the HgTe-like (T_0 -mode) and ZnTe-like (T_1 -mode) sub-band maxima in the case of the $\text{Hg}_{0.80}\text{Zn}_{0.20}\text{Te}$ alloy.

temperatures from 40 K to 300 K. These modes (HgTe-like in the case of T_0 and CdTe- or ZnTe-like in the case of T_1) constitute more than 98% of the phonon numbers in the lattice, and their temperature behavior may reflect the resonance e - p interaction that occurs under the conditions described above.

There is a clear discontinuity in the temperature behavior of the HgTe-like T_0 -mode phonon frequency at 245 K (Fig. 3). There is an additional discontinuity at 285 K. According to the behavior illustrated in Fig. 1(a), the inversion of the energy spectrum corresponds to $E_g \equiv \Gamma_6 - \Gamma_8 = 0$, and it occurs at 245 K for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloys. Therefore, an achievement of this point from the negative side $E_g < 0$ (the increase of the temperature from 150 K to 245 K), causes a shift of the transverse optical phonon frequency (the HgTe-like T_0 -mode) to the higher values. On the other hand, when E_g is positive and decreasing, i.e., the temperature decreases from 280 K to 245 K, ω_{TO} decreases.

This experimental behavior can be described by an equation that is derived from equation (3):

$$\omega_{TO}^{*2} = \omega_{TO}^2 \pm \frac{4\Xi_{CV}^2}{Ma^2W} \ln \frac{W}{2E_F + |E_g|} \quad , \quad (5)$$

where E_F is the Fermi energy measured from the band edge, and W is the sum of the widths of the conduction and valence bands.

In (5), “+” corresponds to $E_g < 0$ and “-” corresponds to $E_g > 0$. Therefore, the zero-gap state in the MCT alloys determines a singularity in the phonon spectrum, but it does not determine a “softening” of the phonon mode, as discussed by Kawamura *et al.* [7].

In Fig. 3, two branches of the curves obtained by plotting $\omega_{TO}^* \equiv \omega_{TO}(E_g T)$ for $E_g < 0$ and $E_g > 0$ are shown; equation (5) was used to plot the curves. The calculations were performed using the following parameters: $W = 8$ eV [13] and $E_F = 6$ meV. Although the electron concentration is low, the electron gas is degenerate at the semimetallic state, and

the Fermi level was determined from the abovementioned values of n , with $m_c^* = 0.001m_0$. The optical deformation potential for the interband electron transitions in the area around $k = 0$ (the Γ point) is $\Xi_{CV} = 5$ eV, and this potential is strongly screened by free electrons [13]. In equation (5), $M = 78 \cdot 1.66 \cdot 10^{-27}$ kg, $a = 6.49$ Å [1], and $\omega_{TO}^- = 120.5$ cm⁻¹ for $E_g < 0$. The value of ω_{TO}^- was obtained by extrapolating the $\omega_{TO}^-(T)$ -dependence from 40 to 150 K, as shown in Fig. 3, and $\omega_{TO}^+ = 122.5$ cm⁻¹.

Therefore, equation (5) describes the singularity observed at 245 K in the experimental dependence of $\omega_{TO}(T)$ for the HgTe-like T_0 -mode, although compared to the theoretical curve, the experimental curve is slightly shifted toward higher wavenumbers. In the case of the CdTe-like T_1 -mode, the discontinuity is not as pronounced; this indicates that the optical deformation potential is smaller in this case.

In the case of the Hg_{0.80}Zn_{0.20}Te alloy, there is a discontinuity in the temperature dependence of the HgTe-like mode frequency at 83 K (see Fig. 4). This confirms the existence of the returnable e - p interaction in this alloy at the point $E_g(T) = 0$ (see Fig. 1(a)). We can assume that in case of this compound, the influence of the e - p interaction that causes a deformation on the temperature dependence of the phonon modes is less than that in the case of Hg_{1-x}Cd_xTe.

Acknowledgments

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