Temperature Dependence Discontinuity of the Phonon Mode Frequencies Caused by a Zero-Gap State in HgCdTe Alloys

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In the HgCdTe (MCT) alloys, a zero-gap state $E_g = \Gamma_6 - \Gamma_8 = 0$ may occur as the composition varies from HgTe to CdTe. This singular mechanism of the E_g variation may be triggered by an external pressure or by a temperature. In this Letter, we present experimental data of the optical reflectivity in the far-infrared (FIR) domain in a wide interval of temperature (from 10 to 290 K) of the $Hg_{1-x}Cd_xTe$ ($x = 0.115$) samples. Since the intensity of classical IR sources drops abruptly in this spectral region, a brilliant synchrotron radiation FIR source has been used. The results clearly show that frequencies of the optical phonon modes exhibit discontinuity in their temperature dependence when a zero-gap state occurs.

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Introduction.—The quasibinary HgCdTe (MCT) alloys form a continuous series of $Hg_{1-x}Cd_xTe$ solid solutions when x ranges from 0 to 1 and all of them are characterized by the zinc-blend crystalline structure [1]. In these alloys, a band inversion and, as a result, a zero-gap state $E_g \equiv \Gamma_6 - \Gamma_8 = 0$ occurs as the composition varies from HgTe to CdTe. The appearance of a zero-gap state is also a function of the temperature so that the effective condition to be fulfilled is $E_g(x, T) = 0$. According to the Kane's theory [2] for the compositions with a zero-band gap, the electron effective mass m_c^* at the conduction band edge is close to zero. Many physical properties are then strongly affected by this singular characteristic of the band structure of such alloys.

At a zero-gap state, the dielectric function has a peculiar behavior as well; it reaches a maximum, i.e., the so-called ''anomaly of the dielectric constant'' [1] that addresses a significant role of the electron-phonon interaction in the dielectric properties of crystals.

In this Letter, we present and discuss the optical reflectivity spectra of the $Hg_{1-x}Cd_xTe$ ($x = 0.115$) samples collected in the far-infrared region (FIR) in a wide temperature range. The analysis will clearly show the presence of a discontinuity of frequencies of the optical phonon modes when a zero-gap state occurs.

Theory.—To analyze the influence of the zero-gap state to the phonon spectra, it is necessary to identify the electron-phonon interaction mechanism that is responsible for the dramatic change of the phonon frequency. Actually, a deformation of the potential that is responsible for the interaction of electrons with the transverse optical phonons (TO-phonons), is the preferred mechanism because only TO-phonons are clearly recognized in the optical reflectivity experiments.

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

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

where n and n' are the Bloch states and s is an index of the phonon modes. $\Xi_{n,n'}(k, q)$ is the optical deformation potential matrix 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 cell 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 (cation and anion dipole pair: in the case of the HgTe-modes, the Hg and Te atoms, respectively), and a is the lattice constant.

We are interested in the deformation potential matrix elements only between the valence and the conduction band. Therefore, following Ref. [4], the self energy of the TO-phonons with small wave vector q is given by the formula

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

where E_g is the energy gap and

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

$V_{cv}(k, q)$ in Eq. (4) does not depend on the wave vector of

the long-wave optical phonons ($q \approx 0$), thus $E_c(k+q) - E_v(k) = E_g$.

Two kinds of singularity we can recognize in Eq. (3): the first one, when E_g is equal to $\hbar\omega_{\mathrm{TO}}$, and the second one, when E_g equals zero. In the first case, the splitting of the optical phonon frequency dependence $\omega_{\mathrm{TO}}(T)$ should take place when the electron-phonon interaction couples two electron states (Γ_6 and Γ_8) so that some "pinning" effect could appear at $\hbar\omega_{\mathrm{TO}} = E_g$ due to the anticrossing of two interacted states. A principally different effect is expected for the $\omega_{\mathrm{TO}}(T)$ dependence in the second case, i.e., at the temperature when $E_g(T) = 0$. 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 goes to zero from the positive side of the energy gap (a normal band structure). Hence, a discontinuity in $\omega_{\mathrm{TO}}(T)$ could occur at $E_g(T) = 0$, whereas, according to the Ref. [4], only a softening of the phonon optical modes is supposed to occur with the frequency decreases.

In Fig. 1, the temperature dependence of $E_g(T)$ for the solid solution $Hg_{1-x}Cd_xTe$ ($x = 0.115$) has been calculated using the empiric formula [5] of

$$E_g(x,T) = -0.303 + 1.73x + 5.6\cdot 10^{-4}(1-2x)T + 0.25x^4 \tag{5}$$

that was well verified experimentally [1,6]. In Fig. 1, we also show the ω_{TO}-phonon frequency values of the HgTe- and CdTe-like modes for such HgCdTe [7] composition. Additional details are discussed in the Section IV. It should be emphasized that the conditions $\hbar\omega_{\mathrm{TO}} = E_g$ and $E_g = 0$ occur at 280 and 245 K, respectively.

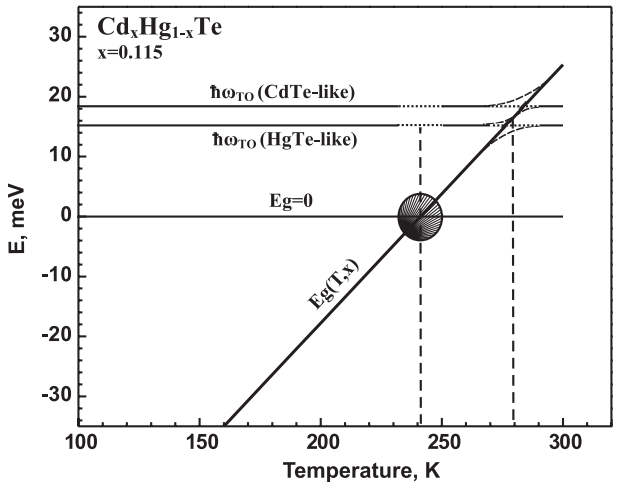

FIG. 1. Temperature dependence of $E_g(T)$ for $Hg_{1-x}Cd_xTe$ ($x = 0.115$) samples calculated according to the empirical formula (5) and positions of the expected singularities: $E_g = 0$ and $E_g = \hbar\omega_{\mathrm{TO}}$.

Experiment.—In order to observe experimentally the effects described above, brilliant intensive synchrotron radiation (SR) in the far infrared region was used. This radiation exhibits unique advantages in comparison with the standard sources, whose intensity actually drops abruptly in this spectral region. The signal to noise ratio and the spectral resolution available with conventional IR sources in the FIR range are also limited and may be not sufficient to resolve the fine structures in the reflectivity spectra associated with the presence of the electron-phonon interaction.

FIR reflectivity experiments were performed at the DAΦNE-light laboratory at Frascati (Italy) using the experimental setup described in Ref. [8]. We used a BRUKER Equinox 55 FT-IR interferometer modified to collect spectra in vacuum. As IR sources, both the synchrotron radiation from the DAΦNE storage ring and a mercury lamp were used. Measurements were performed in a temperature range of 20–300 K and in the wave number domain from 50 to 600 cm^{-1}. In order to provide the spectral resolution of 1 cm^{-1} (2 cm^{-1} in some cases), we typically collected 200 scans within 600 s of acquisition time with a bolometer cooled to 4.2 K. The reflectivity was measured using as a reference a gold film evaporated onto the surface of the investigated samples. This method enabled us to measure the reflectivity coefficient with an accuracy of about 0.2%.

The $Hg_xCd_{1-x}Te$ crystals were grown at the Institute of Physics Polish Academy of Sciences in Warsaw. We used for the zero-gap state study a sample with composition $x = 0.115 \pm 0.005$ annealed at 250 °C in a Hg-atmosphere to obtain a n-type sample with a low level of Hg vacancies, $n \approx 6.5 \times 10^{14}$ cm^{-3} and $\mu = 2.8 \times 10^5$ $\mathrm{cm}^2/\mathrm{Vs}$ at 77 K. The homogeneity of this sample was controlled by the x-ray microprobe analysis. The CdTe alloy composition (x) was varied less than 0.5% over the ingot length of 4 mm.

The measured curves of $R(\omega, T)$ for $Hg_{0.885}Cd_{0.115}Te$ in the frequency region from 80 cm^{-1} to 170 cm^{-1} and in the temperature interval 40 K–300 K are shown in Fig. 2. From Fig. 2, it is clearly seen that the main phonon band consists of two sub-bands: a HgTe-like band in the range of 118–135 cm^{-1} and a CdTe-like band in the range of 140–160 cm^{-1}, and both of them are characterized by a fine structure [7]. A nonmonotonic temperature dependency of the reflectivity maxima can be seen, too. To recognize the real frequency positions of a phonon modes, it is necessary to calculate the imaginary part of the dielectric function.

We calculated the imaginary part of the dielectric function from the reflectivity spectra shown in Fig. 2, by means of the Kramers-Kronig (KK) procedure with an estimated uncertainty of about 1.5% for all experimental data. The results are shown in Figs. 3(a) and 3(b) where the $\mathrm{Im}[\epsilon(\omega, T)]$ curves of the $Hg_{0.885}Cd_{0.115}Te$-sample are

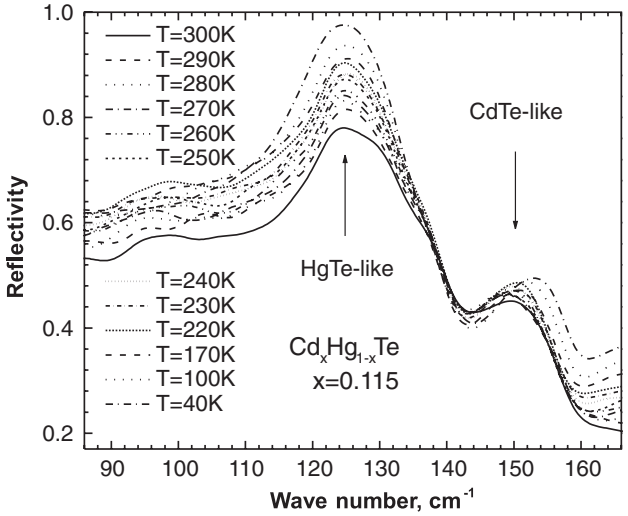

FIG. 2. Reflectivity spectra for $Hg_{1-x}Cd_xTe$ ($x = 0.115$) in the frequency region from 80 to 180 cm^{-1} in the temperature region 40 –300 K.

compared at different temperatures. We have to underline here that a maximum of the HgTe-like sub-band is shifted towards higher frequencies when the temperature increases from 170 to 240 K, while for temperatures higher than 240 K, the maximum is shifted to lower frequencies. Some nonmonotonic temperature dependence of the CdTe-like sub-band maximum frequency positon, near 245 K is observed too. The frequency positions of the HgTe-like and CdTe-like sub-band maxima of the Im$[\epsilon(\omega, T)]$ curves at different temperatures in the interval 40–300 K are shown in Fig. 4.

Discussion.—The $Hg_{1-x}Cd_xTe$ crystalline structure is characterized by tetrahedra, each with a central ion surrounded in the first coordination shell by four nearest neighbors (NN) at the vertices. Verleur and Barker [9] studying the $GaAs_yP_{1-y}$ system, explained the vibrational spectra of a ternary solid solution in terms of five basic elemental tetrahedra. In the $A_xB_{1-x}Z$ ternary tetrahedron structures, different tetrahedron configurations T_n (n is the number of B-atoms in the tetrahedron) coexist simultaneously: two strictly binary ones corresponding to the AZ and the BZ compounds, whose lattices are characterized by the tedrahedron units T_0 and T_4 (configurations), respectively, and 3 strictly ternary ones actually characterized by the configurations T_1, T_2, and T_3. In an ideal crystal lattice, they generate altogether at least $(2 \times 1) + (3 \times 2) = 2 + 6 = 8$ optically active phonon modes. These are canonical phonon modes (CPMs) [10], some of which, as mentioned above, appear as fine structure of the two bands lying in the ranges 118–135 cm^{-1} and 140–160 cm^{-1} as showed in Figs. 3(a) and 3(b).

In our case, when $x = 0.115$, the T_0 component dominates in the crystal lattice and the corresponding mode in the HgTe-like sub-band is the strongest one and determines

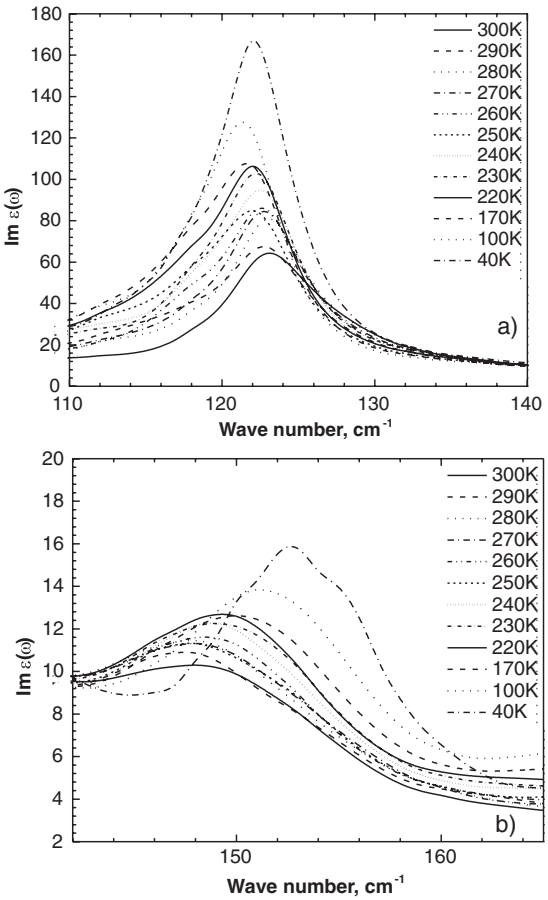

FIG. 3. Imaginary part of dielectric function Im$[\epsilon(\omega, T)]$ calculated from reflectivity spectra of $Hg_{1-x}Cd_xTe$ ($x = 0.115$) samples (Fig. 2) by Kramers-Kroning transformation in the region 110–140 cm^{-1} (a) and in the region 142–165 cm^{-1} (b).

the maximum of this sub-band. For the CdTe-like sub-band the CdTe oscillations in the T_1-tetrahedra induce the maximum. Therefore, as is shown in Fig. 4, the frequency positions of the sub-bands maxima are really these two modes frequencies at different temperatures in the range from 40 to 300 K. These two modes constitute more then 98% of the phonon numbers in the lattice, and their temperature behavior may reflect the resonance electron-phonon interaction which occurs at the conditions described in the Section II.

A clear discontinuity in the temperature behavior of the HgTe-like T_0-mode phonon frequency exists at 245 K. An additional discontinuity is present also at 285 K. According to the behavior described in Fig. 1, the inversion of the energy spectrum corresponds to $E_g \equiv \Gamma_6 - \Gamma_8 = 0$, occurs at the temperature 245 K. Therefore, an achievement this point from the negative side $E_g < 0$ (the increase of the temperature from 150 to 245 K) causes a shift of the transverse optical phonon frequency (the HgTe-like T_0-mode) to higher values, while the diminishing of the energy gap from the positive side $E_g > 0$ (the decrease of

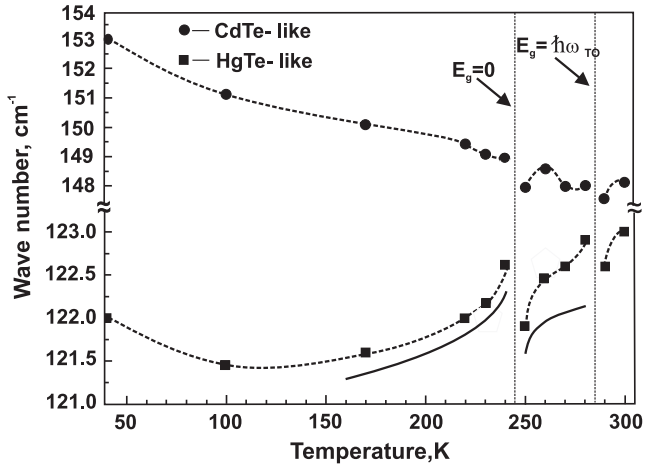

FIG. 4. Plot of the frequency positions in the wave number vs temperature range of the HgTe-like (T_0-mode) and CdTe-like (T_1 mode) sub-band maxima on the Im$[\epsilon(\omega, T)]$ curves [Figs. 3(a) and 3(b)]. The solid curves are calculated according Eq. (6) (more details in text).

temperature from 280 K to 245 K) causes a shift of ω_{TO} to smaller values. This experimental behavior can be described by an equation that is derived from Eq. (3):

$$\omega_{\mathrm{TO}}^{*2} = \omega_{\mathrm{TO}}^{2} \pm \frac{4\Xi_{cv}^{2}}{Ma^{2}W} \ln\frac{W}{2E_F + |E_g|}, \qquad (6)$$

where E_F is the Fermi energy measured from band edge and W is the sum of the conduction and valence band width. The sign "+" in (6) corresponds to $E_g < 0$ and the "−" one is for $E_g > 0$. As a consequence, the zero-gap state in the MCT alloys determines a singularity in the phonon spectrum but not a "softening" of the phonon mode as was discussed by Kawamura *et. al.* [4].

In Fig. 4, two branches of the $\omega_{\mathrm{TO}}^{*} \equiv \omega_{\mathrm{TO}}(E_g(T))$ curves for $E_g < 0$ and $E_g > 0$, have been calculated according to (6). Calculations were performed using the following parameters: $W = 8$ eV [11], $E_F = 6$ meV. Although the electron concentration is low, the electron gas is degenerate at the semimetallic state, and the Fermi level has been determined from the above mentioned values of n and with $m_c^{*} = 0.001 m_0$. The optical deformation potential for the interband electron transitions in the area around $k = 0$ (Γ-point) is $\Xi_{cv} = 5$ eV, and it is actually strongly screened by free electrons [12], In Eq. (6), $M = 78 \times 1.66 \times 10^{-27}$ kg, $a = 6.49$ Å [1], and $\omega_{\mathrm{TO}}^{-} = 120.5$ cm^{-1} for $E_g < 0$. The $\omega_{\mathrm{TO}}^{-}(T)$ value has been obtained by the extrapolation of the $\omega_{\mathrm{TO}}^{-}(T)$ dependence from 40 to 150 K, as is shown in Fig. 4, and the value of $\omega_{\mathrm{TO}}^{+} = 122.5$ cm^{-1}.

Therefore, Eq. (6) describes the singularity observed at 245 K in the experimental dependence of the $\omega_{\mathrm{TO}}(T)$ for the HgTe-like T_0-mode, although the experimental curve is slightly shifted to higher wave numbers with respect to the theoretical one. In case of the CdTe-like T_1-mode, the discontinuity is not so pronounced what indicates a smaller optical deformation potential. That causes a smallest influence on the phonon mode.

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