Defect activated infrared multiphonon excitation in iron-doped semi-insulating indium phosphide

Lung-Han Peng,[a] Tom Broekaert, Woo-Young Choi, Clifton Fonstad, and Victor Jones[a]
Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Multiphonon excitation induced by long-range order crystal-field and short-range order Jahn–Teller distortion effects is observed in Fe-doped semi-insulating InP in the spectral range from 400 to 1100 cm^{-1} for infrared light propagating in a slab waveguide geometry. Transmission measurement data are analyzed in terms of phonon energies at critical points in the Brillouin zone. The phonon energies obtained are in excellent agreement with recently reported second order Raman scattering spectra and two-phonon absorption measurements of crystalline InP. The energy differences between the nearly degenerate two phonon transverse optical + longitudinal optical transitions at the Γ, X, and L points are also resolved and shown to be 10 cm^{-1}. No localized mode or vibronic level absorption is observed, consistent with the relatively low concentration of Fe impurities in the samples.

Fe-doped semi-insulating indium phosphide (SI InP) has drawn special attention recently because of its application in high speed devices and optoelectronics. In many infrared optoelectronics applications a waveguide geometry is utilized, which involves in a long optical path in the material and increases the significance of even very weak optical absorption processes. It is therefore important to understand the infrared absorption processes occurring in InP and to access their impact on devices. We report here the first study of weak defect-induced multiple-phonon absorption in Fe-doped SI InP in the range from 400 (25 μm) to 1100 cm^{-1} (10 μm).

It is well known that introducing impurities in an otherwise perfect crystal destroys translational invariance and lowers the symmetry from space group symmetry to point group symmetry.[1,2] One of the most important results induced by this reduction in symmetry is that all the lattice vibration modes become infrared and Raman allowed. An infrared (IR) absorption measurement is consequently able to map the phonon density spectrum of all possible phonon overtone and combination modes.

The nature of the host material and the impurities also play an important role in determining the IR absorption spectrum. It is well understood, for example, that in heavily transition metal doped II-VI zinc blende structures (e.g., Fe-doped ZnS), the long-range crystal field will split the impurity ground electronic states into a doublet and a triplet.[3–5] Furthermore, dynamic Jahn–Teller distortion will strongly affect the coupling between the lattice vibration and the interimpurity electronic ground states (vibronic levels) and will induce phonon sidebands in low temperature absorption and photoluminescence (PL) measurements.[3–5] Although the validity of applying the crystal field theory to the more covalent III-V compound materials has been questioned, recent PL and absorption studies of vibronic level transitions between the transitio metal electronic ground states in Cr-doped GaAs and Fe doped InP strongly support the validity of applying th crystal field theory in transition-metal-doped III-V compounds.[6–12]

There have been several reports on the phonon excita tion spectrum for undoped bulk InP in the spectral rang from 400 to 700 cm^{-1} based on measurements of secon order Raman scattering,[13,14] IR two-phonon absorption, and inelastic neutron scattering.[16] However, none of th work has been done on Fe-doped SI InP, and no measur ments beyond 700 cm^{-1} have been reported. The purpo of this work is (i) to investigate the lattice absorption fro 400 to 1100 cm^{-1} in a long optical path slab waveguic geometry, and (ii) to confirm the accuracy of recently pu lished phonon enegies measured from second ord effects[13–15] by comparing them with multiphonon absor tion measurements.

Fast Fourier transform infrared (FTIR) measur ments were performed on commerical Fe-doped SI In with a resistivity in excess of 10^6 Ω cm and a correspon ing iron concentration of approximately 10^{16} cm^{-3}. FTIR spectrometer with a mercury cadmium telluri (MCT) detector and spectral resolution of 4 cm^{-1} w used for the measurements. Room-temperature transm sion measurement data are shown in Figs. 1 and 2, resp tively, for light incident normal to the sample surface a for light propagating in the plane of the sample, i.e., in slab waveguide geometry. The absorption peak positio and their assignments are tabulated in Table I. Comparis of the phonon energies determined in this work with t previously published values is presented in Table II.

The absorption spectra in Figs. 1 and 2 were measur in two configurations having much different optical pa lengths, and allow one to observed infrared absorption pr cesses spanning a wide intensity range. The data in Fig. which were measured with normal incidence, provide formation on the relatively strong absorption proces which occur in InP between 400 and 700 cm^{-1} and ha

[a]Division of Applied Sciences, Harvard University, Cambridge, MA 02138.

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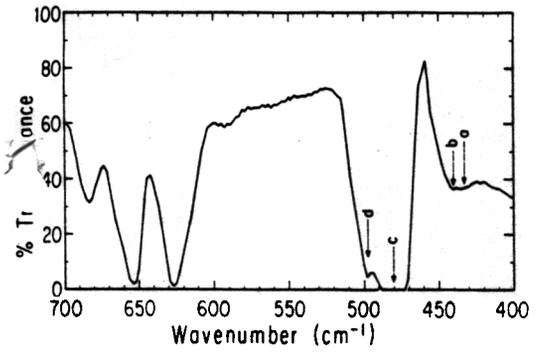

FIG. 1. The transmission spectrum of Fe-doped indium phosphide between 400 and 700 cm^{-1} measured at 300 K with light incident normal to the surface of the sample. The identification of the peaks is given in Table I.

been reported previously in the literature.[13–15] The peaks ranging from 400 to 500 cm^{-1} (*a* through *d*) are associated with *K* and *W* singular points in the Brillouin zone.[14,15] The three strong peaks between 600 and 700 cm^{-1} are due to two-phonon processes involving, respectively, two transverse optical (TO) phonons, a TO and a longitudinal optical (LO) phonon, and two LO phonons. Careful examination of the shapes of these three absorption peaks hints that each may be the superposition of several peaks. However, each of the two-phonon transitions are nearly degenerate at the Γ, *X*, and *L* points and the small energy differences between the transitions occurring at these critical points are normally unresolvable at normal incidence.

The data in Fig. 2, which were measured in the waveguide geometry, provide information on weaker absorption (multiple phonon) processes. It also helps to resolve the strong two-phonon processes seen in Fig. 1. It is clearly seen from Fig. 2 that the three strong two-phonon processes observed in Fig. 1 are now well resolved into nine individual absorption peaks. We observe a 10 cm^{-1} energy difference between the nearly degenerate two phonon transitions occuring at the Γ, *X*, and *L* points. It is believed this is due to the Jahn–Teller distortion effect; this point is under continued investigation.

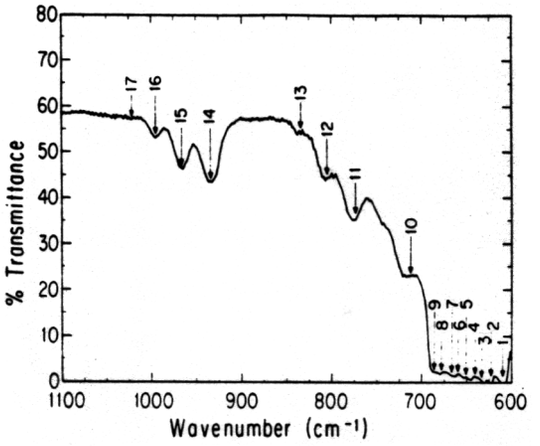

FIG. 2. The transmission spectrum of Fe-doped indium phosphide between 600 and 1100 cm^{-1} measured at 300 K with light propagating in the plane of the sample, i.e., in a slab waveguide geometry. The identification of the peaks is given in Table I.

TABLE I. Phonon state assignments in the transmission spectra of Fe-doped InP at 300 K.

	Intensity	Frequency (cm^{-1})	Assignment
a		430	(*K*, *W*)
b		440	(*K*, *W*)
c		480	(*K*, *W*)
d		500	(*K*, *W*)
1		610	2TO(Γ)
2		625	2TO(*L*)
3		631	2TO(*X*)
4		639	LO + TO
5		645	LO + TO
6		655	LO + TO
7		670	2LO(*X*)
8		680	2LO(*L*)
9		690	2LO(Γ)
10		725	2TO(Γ) + 2TA(*L*)
11		775	2TO(Γ) + 2LA(*L*)
12		810	TO(Γ) + LO(Γ) + 2LA(*L*)
13		840	2LO(Γ) + 2LA(*L*)
14		930	2TO(Γ) + 4LA(*L*)
15		970	TO(Γ) + LO(Γ) + 4LA(*L*)
16		1000	2LO(Γ) + 4LA(*L*)
17		1025	3LO(Γ)

Multiple phonon excitation is seen clearly from 700 to 1100 cm^{-1} and the corresponding phonon state assignments are listed in Table I. The most obvious features are two sets of replicas of the three two-phonon absorption peaks that are so prominent to the left in Fig. 1 (and which are resolved into nine closely spaced peaks in Fig. 2). The first set, peaks 11, 12, and 13, are approximately 160 cm^{-1} away from the lower energy peaks. This separation corresponds to two longitudinal acoustic (LA) phonons. A constant phonon energy shift of 160 cm^{-1} is also found between the pairs of absorption peaks 11 and 14, 12 and 15, and 13 and 16, which indicates that the higher energy set of peaks is a replica of the first involving an additional two LA phonons. It is worth noting that momentum conservation of the incident IR light requires increments of two

TABLE II. Experimental phonon frequencies (cm^{-1}) in InP at 300 K.

		Raman[a]	Raman[b]	IR absorption[c]	This work
Γ	TO	304.5±0.3	306.0±0.5		
	LO	3464±0.3	348.5±0.5		
L	TA	54±1	55±0.5	55±3	52±2
	LA	82±1	168±2	168±2	80±2
	TO	246±2	312±2	313±1	312±2
	LO	341±2	344±2	341±1	340±2
X	TA	67±1	68±0.5	64±3	
	LA	125±1	190±4	191±2	
	TO	282±2	320±2	317±1	315±2
	LO	315±2	334±2	336±3	335±2

[a]Reference 13.
[b]Reference 14.
[c]Reference 15.

phonons for each replica set. It is also not surprising that the low energy acoustic phonon branch, i.e., LA(L), would dominate in the multiphonon excitation spectrum because of the change of force constants and the lattice distortion along the (111) direction in a zinc blende structure. Peak 10 is located 50 cm^{-1} lower than peak 11 [2TO(Γ) + 2LA(L)] and is tentatively assigned to be 2TO(Γ) + 2TA(L). Peak 17 is 335 cm^{-1} higher than peak 9 [2LO(Γ)] and is tentatively assigned to be a 3LO(Γ) process. The 3LO(Γ) process, peak 17, is weak because the cubic term in the Hamiltonian is very small due to the lack of inversion symmetry in zinc blende structures.

From the tentative assignments listed in Table I, we can solve for the critical point phonon energies. Self-consistent critical point phonon energies obtained from the replica sets are listed in Table II. Excellent agreement is found when comparing the present results with previously published data.[13,14] The self-consistently solved TA(L) phonon energy is in excellent agreement with the previously published data.[13–15] This confirms that the LA(L) phonon energy is 80 cm^{-1} (Ref. 13) rather than 160 cm^{-1}.[14,15]

As was mentioned in the introduction, the electromagnetic wave interaction with the symmetry-broken crystal is now modified by the long-range crystal-field and short-range Jahn–Teller distortion which only preserves the point group symmetry T_d of the zinc blende structure. By transforming the perturbation Hamiltonian into a normal mode representation, and after second quantization, it is easy to show that, in addition to the two phonon process, three and four phonon processes are now possible. Considering the conservation of incident photon momentum, the excitation of zone center phonons (Γ) and phonons from opposite directions at the zone boundaries (X, L, and K from equivalent phonon branches in the Brillouin zone) is expected. These expectations are in agreement with the experimental observations in Fig. 2 and the assignments in Table I.

It should be pointed out that according to the Brout sum rule,[15,17] the sum of any optical branch phonon energies is constant and independent of the phonon wave vector for purely electrostatic interatomic forces and for short range forces between the nearest neighbors. Though the Fe ions substitute on In sites, and change the interatomic force constant, this perturbation does not seem to change the lattice vibration. One of the reasons is that the Fe doping concentration is very low. Therefore localized mode and internal vibronic level excitations are too weak to be observed. Experimentally, to see the localized modes and vibronic levels excitation, a doping concentration as high as 10^{19} cm^{-3} is required.[6,12]

In conclusion, defect-activated multiphonon excitation in Fe-doped SI InP has been observed in a slab waveguide geometry in the frequency range from 400 to 1100 cm^{-1}. Translational symmetries broken by substitutional impurities and modulation of the electromagnetic wave interactions by crystal field and lattice distortion lead to multiphonon (n = 3,4,6) absorption which is not observed in a traditional short path normal incidence geometry. LA(L) phonons are seen to dominate the multiphonon excitation spectrum due to the distortion along the (111) direction. The phonon energies obtained at the critical points were found to be in excellent agreement with recently published data. An energy difference of 10 cm^{-1} was observed at 650 cm^{-1} between the nearly degenerate two-phonon TO + LO transitions at the Γ, X, and L points in InP. Consistent with the low Fe concentration in the indium phosphide samples, no localized mode and inter-vibronic level excitation was observed.

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[1] R. Loudon, Proc. Phys. Soc. **84**, 379 (1964).
[2] J. L. Birman, Phys. Rev. **131**, 1489 (1963).
[3] G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. **152**, 376 (1966).
[4] F. S. Ham and G. A. Slack, Phys. Rev. B **4**, 777 (1971).
[5] J. T. Vallin, G. A. Slack, S. Roberts, and A. E. Hughes, Phys. Rev. B **2**, 4313 (1970).
[6] W. H. Koschel, U. Kaufman, and S. G. Bishop, Solid State Commun. **21**, 1069 (1977).
[7] G. K. Ippolitiva, E. M. Omel'yanovskii, N. M. Pavlov, A. Ya. Nashel-'skii, and S. Y. Yakobson, Sov. Phys. Semicond. **11**, 773 (1977).
[8] D. C. Look, Phys. Rev. B **20**, 4160 (1979).
[9] D. C. Look, Solid State Commun. **33**, 237 (1980).
[10] G. K. Ippolitiva and E. M. Omel'yanovskii, Sov. Phys. Semicond. **9**, 156 (1975).
[11] P. W. Yu, Solid State Commun. **32**, 1111 (1979).
[12] B. Deveaud, G. Picoli, B. Lambert, and G. Martinez, Phys. Rev. B **29**, 5749 (1984).
[13] G. F. Alfrey and P. H. Borcherds, J. Phys. C **5**, L272 (1972).
[14] E. Bedel, G. Landa, R. Carles, J. P. Redoules, and J. B. Renucci, J. Phys. C **19**, 1471 (1986).
[15] B. Ulrich and E. Jahne, Phys. Status Solidi B **74**, 601 (1976).
[16] P. H. Borcherds, G. F. Alfrey, D. H. Saunderson, and A. D. B. Woods, J. Phys. C **8**, 2022 (1975).
[17] R. Trommer, H. Muller, M. Cardona, and V. Vogl, Phys. Rev. B **21**, 4869 (1980).