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HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF SHALLOW ACCEPTORS IN ULTRA-PURE GERMANIUM *

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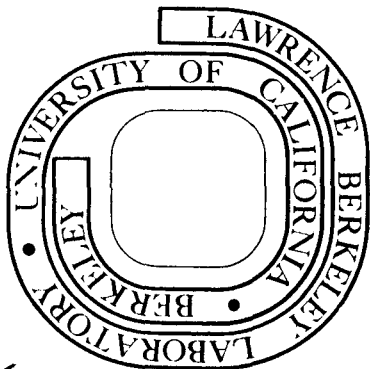
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ABSTRACT

The excitation spectra of shallow acceptors in ultra-pure germanium (10^9 cm^{-3} < N_A - N_D < 10^{12} cm^{-3}) were studied using Fourier Transform Spectroscopy and photothermal excitation. Using samples with a total number of less than 10^8 acceptor atoms, the signal to noise ratio was better than 100. In the purest samples the natural width of some excited states was found to be below the instrumental resolution of 0.03 meV (= 0.25 cm^{-1}). Some new observations involve the resolution of new lines of states near the top of the valence band and the discovery of two unknown shallow acceptors.

HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY
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The recent developments in the purification methods for germanium[1,2] have led to net-impurity concentrations of below 10^9 cm^{-3} with low degrees of compensation. This makes possible higher resolution spectroscopy of neutral acceptors and donors than has been done using considerably less pure material.[3-6] Line broadening[7] due to impurity interaction is found to be negligible. The combination of photothermal ionization[8-11] and far infrared Fourier Transform Spectroscopy circumvent the low sensitivity and resolution of transmission experiments using grating spectrometers. This was shown recently for shallow donors in ultra-pure germanium.[12] The strong dependence of the thermal ionization of a bound carrier from an excited state into the valence band on energy and temperature makes it possible to study selectively different regions of the excitation spectrum.

We report here the following new results:

a) the highest resolution spectra for the group III acceptors in ultra-pure germanium,

b) the separation of a number of excited states near the valence band,

c) the absence of the transition $(8 + 0) \rightarrow (8 + 1)$ leading to the earlier reported E line (3),

d)   the discovery of two unknown shallow acceptors producing

quasi-hydrogenic spectra like the group III acceptors,

e)   the modulation of the free carrier mobility by optical and

accoustical phonons excited by infrared radiation.

Experimental data were obtained from more than fifty high-purity

germanium samples ranging in volume from 0.1 to 0.6 cm^3 and with net-

acceptor concentrations between 10^9 and 10^{12} cm^3. These samples origin-

ated from 15 different crystals grown by the Czochralski method in our

laboratory. The sample preparation involved cutting with a diamond

saw, lapping and then polishing in white-etchant.[*] Contacts with a

linear current/voltage characteristic down to a temperature of 1.2°K

were obtained by rubbing InGa-eutectic into two opposite faces of the

cubic-shaped samples. (Any kind of diffused or alloyed contacts would

introduce considerably more impurity atoms than were originally in the

bulk.) The samples were mounted in a brass cavity inside a helium

cryostat. A 1/2 inch stainless steel light pipe guided the infrared

radiation from the interferometer to the sample. Cooling was achieved

through a copper rod reaching into the liquid helium. A 68-ohm Allen-

Bradley carbon resistor was used as a temperature sensor. A modified

temperature-controller[13] together with an aluminum encased resistor

(25 ohm/25 watt) stabilized the temperature of the sample within less

than 0.05°K from 4.2°K up to 25°K. Optical excitation of the neutral

acceptors was done with a far infrared Michelson Interferometer.[14]

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* White etchant: HNO_3:HF=3:1

In order to avoid aliasing of spectra[14] the frequency range was limited with black polyethylene sheet and Yoshinaga filters.[15] Using chopped excitation radiation, the bound carriers were raised to their various higher lying states and thence thermally excited to the continuum. The resultant ac-signal was differentially amplified, filtered and synchronously rectified by a lock-in amplifier (PAR-H8). A voltage-to-frequency converter and counter allow further filtering and digitizing of the signal. A PDP-11 computer performed all necessary storage and computations for Fourier transforms.

A typical interferogram is shown in Fig. 1; this was obtained from a crystal whose net-acceptor concentration was $\sim 10^{10}$ cm^{-3}. The 'beat' character of the interferogram originates from the strong C and D lines of neutral aluminum acceptors; these lines are seen in Fig. 2, the transform of Fig. 1. The line width is limited to 0.25 cm^{-1} by the interferometer and electronics. The analysis of the Al-spectrum results in four lines (A_1 to A_4) where two lines (A', A'') were reported earlier.[3] The feature I is resolved into the lines (I_1 to I_8). Corresponding lines were found for boron and gallium. The energies are given in Table 1. The lines L_1 to L_4 are ghosts of the C and D lines and are produced by a small pitch error in the mirror-advance screw.[*] Mechanical adjustments reduced the L lines far below the noise level.

A decrease in temperature reduces the transition probability for holes to go from an excited state into the valence band. At 1.2°K the sharp excitations are suppressed and only the continuum remains. We

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* Ruled gratings produce similar ghosts named after Rowland.

successfully fitted the low energy side of the continuum to the Fermi distribution $f = 1/[\exp(\Delta E/kT) + 1]$, which means that the shape of the continuum near threshold is determined mainly by the electron energy distribution at the top of the valence band ($\vec{k} = 0$) and depends only slightly on the density of states. If we assume that the valence band edge lies at $f = 1/2$ we find for the ground state energy of aluminum $E_{g.s.}$ (Al) = 10.90 ± 0.01 meV. This allows an experimental determination of $E_{g.s.}$ (Al) with spectroscopic methods. The value is 0.10 meV higher than the one deduced by Jones and Fisher[3] using theoretical considerations.

The transition $(8 + 0) \rightarrow (8 + 1)$ (E-line) was not observed by our techniques. This is in contrast to absorption experiments[3] and we have to assume that the excitation probability from a even state into the valence band is much smaller than from an odd state.

A new set of lines (impurity X) lying between those of B and Al were found in samples from crystal 291 (Fig. 3) and their energies are given in Table 1. From a generalization of the experimentally determined dependence of the ground state energies of group III elements on the atomic number Z,[3] we would expect the impurity X to have a Z of about 7 to 9. None of the corresponding three elements are known to produce shallow acceptors in germanium. Oxygen should have been found earlier due to its high solubility in germanium.[16] No conclusive information exists about nitrogen or fluorine. Most probably a more sophisticated argument has to be applied. It was shown recently that donors can pair with multivalent acceptors producing shallower levels than the neutral

unpaired acceptor.[17] None of the unknown lines correspond to those already measured. The possibility that the observed acceptor X is created by a crystallographic defect is small since no correlation between the intensity of the most dominant defects (dislocations) and the line intensities could be found. It appears that the impurity X has a chemical character and segregates during crystal growth towards the tail end. Hall effect and IR-measurements of many samples taken from different sections along the crystal yield a segregation coefficient $k_X \sim 0.05 \pm 0.02$.

A second unknown shallow acceptor (impurity Y) was first observed in a polycrystalline sample from a very high-purity zone refined germanium bar (Fig. 4) and later in two crystals pulled from a quartz, and in one crystal grown from a carbon crucible. In the latter crystal the impurity Y was present at a rather high concentration of $\sim 10^{10}$ cm^{-3}. From Hall effect and IR-measurements we found the segregation coefficient of Y to be $k_Y = 0.9 \pm 0.1$. This means that Y is nearly non-segregating in contrast to the dominant impurity aluminum, which segregats normally in crystals grown from carbon crucibles. This behavior could be explained by an impurity which diffuses out of the carbon crucible into the Ge-melt and quickly reaches its rather low maximum solubility.

It was suggested[18] that interstitial oxygen neighboring a group III element could produce an additional chemical shift of the ground state. Our crystals with the highest oxygen content (2 x 10^{14} cm^{-3}; Li-precipitation method[16]), however, do not show any unknown excitation

levels. It cannot be excluded that crystallographic defects other than dislocations which are quenched in during crystal growth[19] are involved in the creation of the shallow acceptors X and Y.

By going to higher wavenumbers (500 cm^{-1}) and temperatures (17°K) many broad structures appeared in the spectra (Fig. 5). Comparison with optical and accoustical phonon modes[20] suggests that these structures are created by interactions between phonons and free carriers. In this case the electrical signal is not produced by changes in the free carrier concentration, but rather by the modulation of the mobility of the free carriers. That the mobility modulation depends on long-range lattice order (crystal perfection) is shown by the fact that we could not observe these modes in dislocation free material (high-vacancy and vacancy-agglomerate concentration).

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	B	Al	Ga	In	X	Y	Be
$E_{g.s.}$	10.57 ±.01	10.90 ±.01*	11.07 ±.01	11.74 ±.01	10.74 ±.01	12.01 ±.01	24.54 ±.03
I_1	10.534 ±.010	10.864 ±.002	11.018 ±.010				
I_2		10.757 ±.003	10.958 ±.010				(5)
I_3	(1)	10.669 ±.002	(2)	(3)		(3)	
I_4		10.595 ±.003					
I_5	10.198 ±.010	10.533 ±.002	10.674 ±.010				
I_6	10.139 ±.010	10.474 ±.002	10.625 ±.010				24.22 ±.02
I_7	10.048 ±.010	10.382 ±.002	10.536 ±.010	(4)			
I_8	9.989 ±.010	10.32 ±.01	(2)				
A_1	9.863 ±.010	10.198 ±.002	10.360 ±.010	11.033 ±.010		11.32 ±.01	
A_2	9.785 ±.010	10.130 ±.002	10.287 ±.010	10.955 ±.010		11.23 ±.01	23.73 ±.02
A_3	9.655 ±.010	9.995 ±.002	10.152 ±.010	10.828 ±.010		11.12 ±.01	
A_4	9.568 ±.010	9.927 ±.004	10.091 ±.010	10.746 ±.015			
B	9.320 ±.005	9.654 ±.002	9.814 ±.005	10.506 ±.010	9.506 ±.010	10.77 ±.01	23.33 ±.02
C	8.686 ±.005	9.025 ±.002	9.185 ±.005	9.864 ±.005	8.870 ±.010	10.13 ±.01	22.86 ±.02
D	7.936 ±.005	8.272 ±.001	8.437 ±.005	9.113 ±.010	8.114 ±.010	9.38 ±.01	21.91 ±.02
G	6.215 ±.010	6.565 ±.005	6.720	—	—	—	—

* Only $E_{g.s.}$ (Al) is experimentally determined, the other $E_{g.s.}$ were obtained by adding 2.63 meV to the energy of the D transition.

(1) interference with Ga-lines

(2) interference with Al-lines

(3) I_1-I_8 did not exceed the noise level

(4) interference with Ga and In lines

(5) I_1-I_4 did not exceed the noise level

TABLE 1

FIGURE CAPTIONS

Fig. 1. Interferogram obtained from sample #313-.2. Sample volume

V = 0.57/cm^3; N_A - N_D = 10^{10}/cm^3; T = 8.0°K; 1000 sampling

points were recorded in approximately 30 minutes. The "beat"

character of the interferogram is produced by the strong

Al(C) and Al(D) lines.

Fig. 2. Spectrum of sample #313-.2. The labeling of the lines is the

same as in Ref. 3. Sample volume V = 0.57/cm ; N_A - N_D = 10^{10}/cm^3;

T = 8.0°K; 1000 sampling points were recorded in approximately

30 minutes. A region below the Al(D) line is magnified by a

factor of four with the baseline shifted. The aluminum con-

centration exceeds all other impurities (B, Ga) by a factor of

more than 20. The explanation for the lines L_1 through L_4 is

given in the text.

Fig. 3. Spectrum of sample #291-14.0. Sample volume V = 0.47/cm^3;

N_A - N_D = 10^{11}/cm^3; T = 8.0°K; 1024 sampling points were

recorded in 30 minutes. Four impurities are present: X (unknown),

Al, Ga and In. The resolution allows the separation of the Ga(C)

and In(D) lines.

Fig. 4. Spectrum of a polycrystaline sample (bar 61). Sample volume

V = 0.34/cm^3; N_A - N_D is unknown, but below 10^{11}/cm^3; T = 8.0°K;

700 sampling points were recorded in 20 minutes. An unknown

acceptor Y produces the strongest lines in the spectrum. The

same lines were found also in several single crystals.

Fig. 5.   Spectra of sample #289-16.0 at T = 14°K and 17°K.   Sample

volume V = 0.22/cm^3; N$_A$ - N$_D$ = 1.7 x 10^{11}/cm^3.   Phonon modes

excited by broad band IR-radiation change the free carrier

mobility and produce a number of broad features.

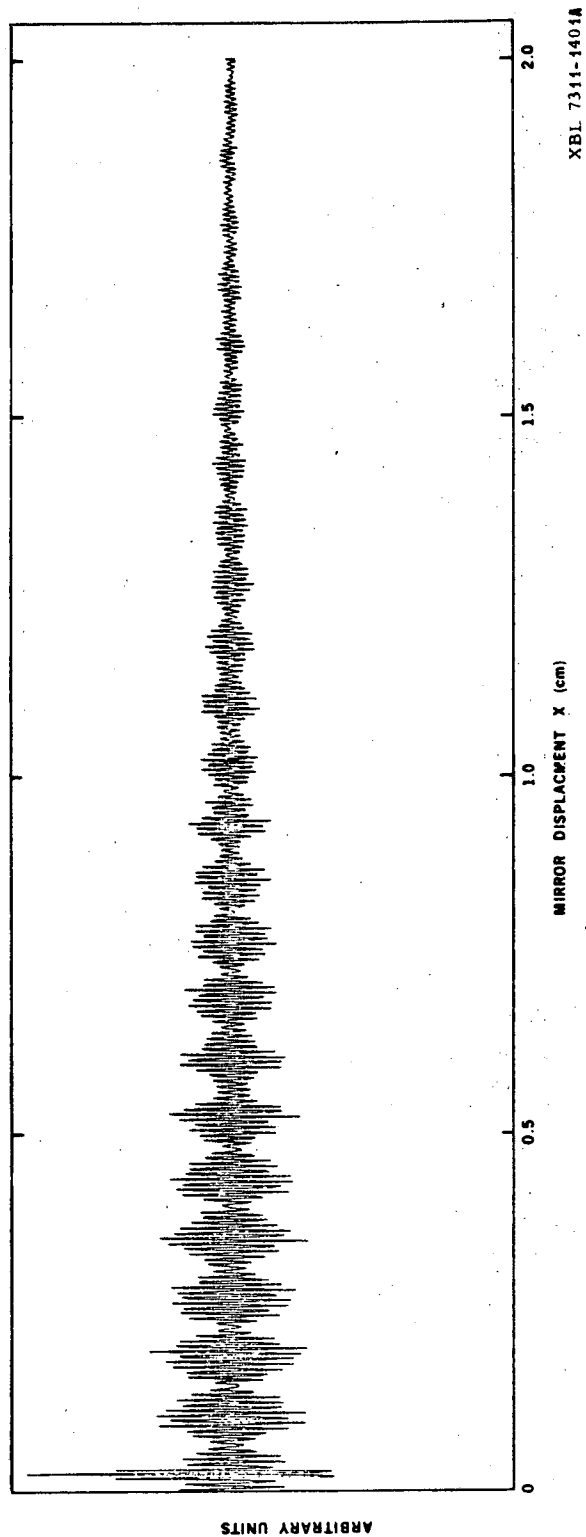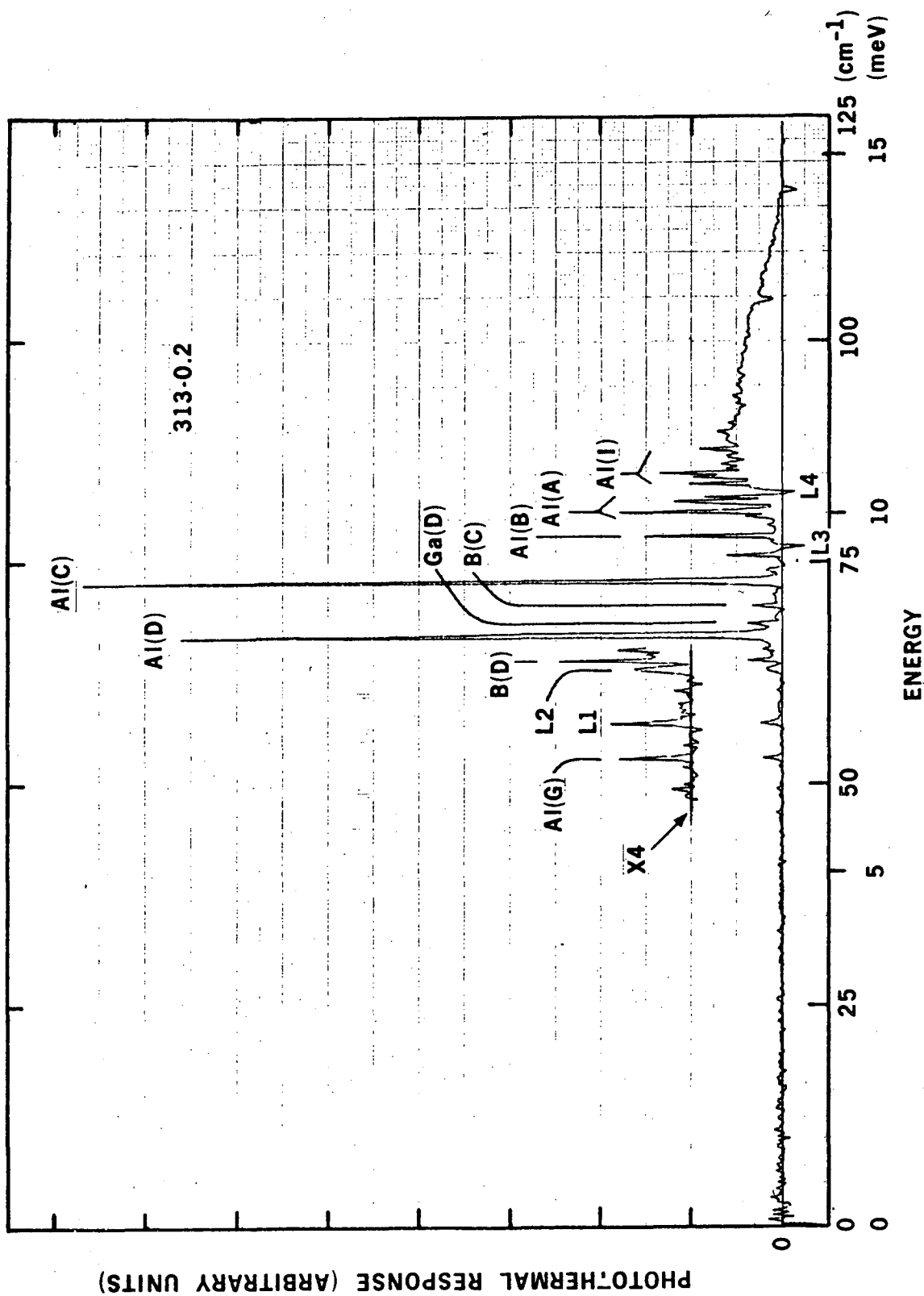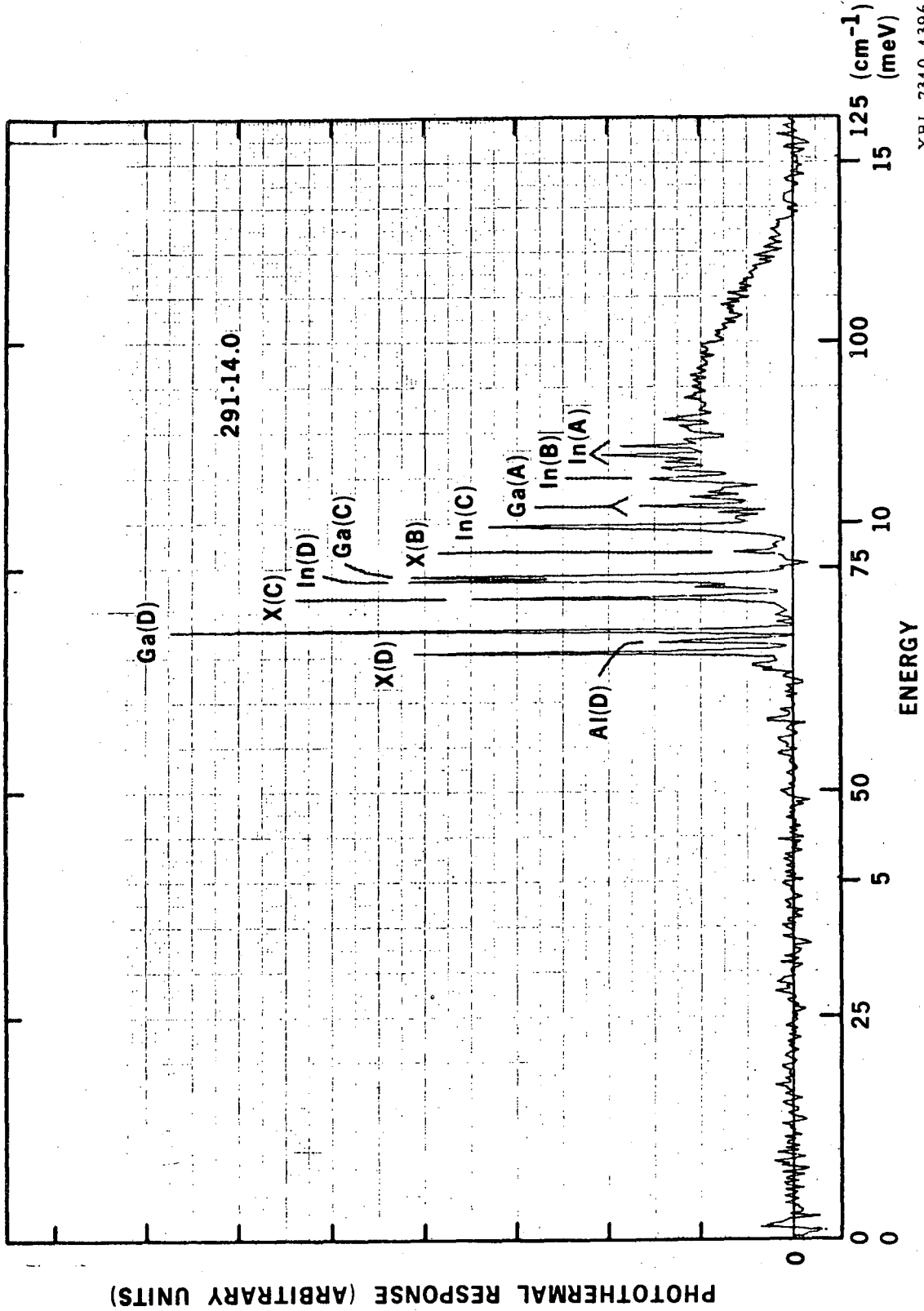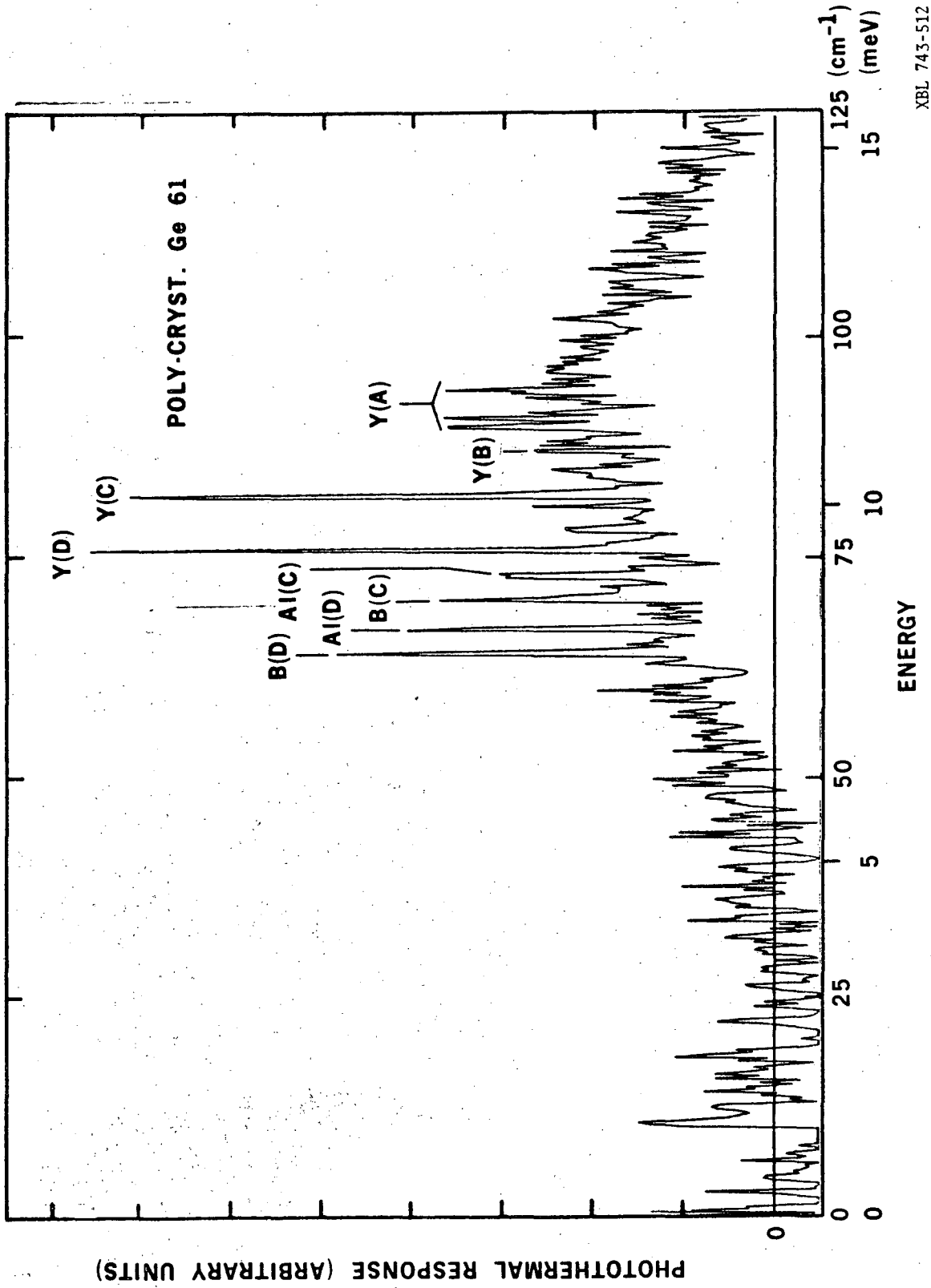MIRROR DISPLACMENT X (cm)

XBL 7311-1401A

ARBITRARY UNITS

Fig. 1

Fig. 2

XBL 7310-1392

XBL 7310-1396

Fig. 3

LBL-2487

Fig. 4

XBL 743-512

Fig. 5