Photoexcited hot electron relaxation processes in n-HgCdTe through impact ionization into traps

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In this article we report on a new type of spectroscopy for impurity and/or defect levels in the energy gap of narrow-gap semiconductors using the near-band-gap photon energies from a laser. This spectroscopy is done under the conditions of intense laser photoexcitation and is associated with the Auger relaxation processes of hot electrons involving impact ionization of valence electrons into impurity or defect levels. Wavelength-independent structure in the photoconductive response versus magnetic field is observed at high intensities in samples of $Hg_{1-x}Cd_xTe$ with $x \approx 0.22$ and 0.24. This structure arises from hot electrons photoexcited high into the conduction band by sequential absorption of CO_2 laser radiation. The hot electrons lose their energy by impact ionizing valence electrons into impurity/defect levels in the gap. For the sample with $x \approx 0.22$ and an energy gap of 95 meV, three levels are found at 15, 45, and 59 meV above the valence band. A level at 61 meV is found for the sample with $x \approx 0.24$ and a gap of 122 meV.

I. INTRODUCTION

The semiconducting $Hg_{1-x}Cd_xTe$ alloys are used extensively as infrared detector materials in a wide range of both civilian and military systems. One of the important challenges in making substantial improvements in the quality and uniformity of the material is to develop better characterization techniques for the detection and identification of defects and impurities. Even though a large effort has been expended in characterizing these levels, most still remain rather poorly understood. Consequently, any new techniques or methods that can be developed to detect and characterize these levels should be exploited. Here we report a new method for observing and studying impurity/defect levels in narrow-gap semiconductors. This new method involves the combined use of intense laser radiation and the techniques of magneto-optical spectroscopy. Structure is observed in the photoconductive (PC) response as a function of magnetic field, the peak positions of which are independent of laser photon energy.

There have been a number of previously observed effects in semiconductors where resonance positions do not depend upon photon energy such as the magneto-impurity effect and the impurity-shifted magnetophonon effect.[1] Hot-electron conditions always seem to be necessary for observing these resonances, and they are achieved either by the non-ohmic conditions created by applying large enough electric fields or else by photoexcitation of carriers deep into the conduction band by optical excitation across the band gap. These effects are therefore distinct from intrinsic and extrinsic oscillatory photoconductivity effects which have been studied in many semiconductors at zero magnetic field. Magneto-impurity resonances (MIRs) have been seen in n-GaAs, n-InP, n- and p-Ge, and n-CdTe.[1] These resonances arise from inelastic scattering processes whereby a free carrier resonantly exchanges energy with a second carrier bound to a shallow acceptor or donor impurity in the presence of a magnetic field. Impurity-assisted magnetophonon resonances arise from a process whereby an electron emits a longitudinal optical (LO) phonon in falling from a Landau level into a bound state of an impurity.

In this work, the near-band-gap photon energies from a CO_2 laser are used to perform a new type of spectroscopy for characterizing impurity/defect levels that differs from the magneto-impurity and the impurity-shifted magnetophonon effects. This spectroscopy is done under the conditions of intense laser photoexcitation and is associated with the Auger relaxation processes of hot conduction band electrons relaxing by impact ionization of valence electrons into impurity levels. This work is important because it provides a new technique for studying impurity/defect levels in narrow-gap semiconductors in which these levels have been generally difficult to measure.

II. EXPERIMENTAL

The experiments reported here were carried out on two single-crystal, bulk grown n-type samples of $Hg_{1-x}Cd_xTe$ with x values of approximately 0.22 and 0.24. Both samples were lapped with alumina grit and then chem-mechanically polished using a 2% bromine–methanol solution. Electrical contacts were made to the samples using pure indium. The magneto-optical system used has been described elsewhere (See Fig. 1 of Ref. 2). Light from a grating tunable continuous wave (cw) CO_2 laser was focused onto a sample placed in a superconducting-magnet/variable temperature dewar system (0–12 T). To prevent lattice heating, the light was mechanically chopped at a low duty cycle of $\approx 1\%$. The propagation direction of the linearly polarized laser light was parallel to the magnetic field. The photoconductive response of the samples was obtained under constant current, ohmic conditions. The magneto-optical spectra (PC response versus magnetic field) were obtained using either ac magnetic field modulation and lock-in amplifier techniques or boxcar averager methods.

III. RESULTS AND DISCUSSION

The interaction of laser radiation with semiconductors is in general a complex phenomenon involving many different types of processes occurring before equilibrium is regained. Which particular processes dominate or are important depend upon such parameters as the laser photon energy, laser intensity, laser pulse width, sample temperature, and sample doping. Illumination of semiconductors with intense radiation also leads to carrier heating effects. Laser-based magneto-optical spectroscopy permits the study of this interaction of laser radiation and allows the observation of a number of separate features or resonances in the PC response versus magnetic field. These features must be understood and appreciated in order to be able to interpret our new high-intensity structure. As shown in Fig. 1 for a sample with $x \approx 0.24$ and a low-temperature band gap of $E_g = 122$ meV, four different features are observed in the spectra, depending upon which combination of laser wavelength, magnetic field range, laser intensity, and lattice temperature is used. First, a two-photon absorption structure is seen at long wavelengths, high intensities, and high magnetic fields. These two-photon magneto-optical spectra have been extensively studied by us in a number of samples of HgCdTe, and this structure is now well understood.[2] At shorter wavelengths, lower magnetic fields, and low laser intensities two sets of magneto-optical structure are observed and identified by upward pointing arrows: a one-photon magneto-absorption (OPMA) structure and a broad impurity magneto-absorption (IMA) peak just to the high field side of the largest OPMA peak. This IMA peak has been attributed to electron transitions from a shallow acceptor to the lowest conduction band Landau level.[2,3] These three sets of resonant structures (one-photon, two-photon, and impurity) can be understood by a Landau-level model (where peaks in the density-of-states occur at energies corresponding to the extremum of each Landau level) along with the corresponding optical transitions.[4] At these peaks there are enhanced optical transition rates or electron scattering rates. The resulting optically created electrons in the conduction band then cause an increase in the conductivity or photoconductive response of the samples.

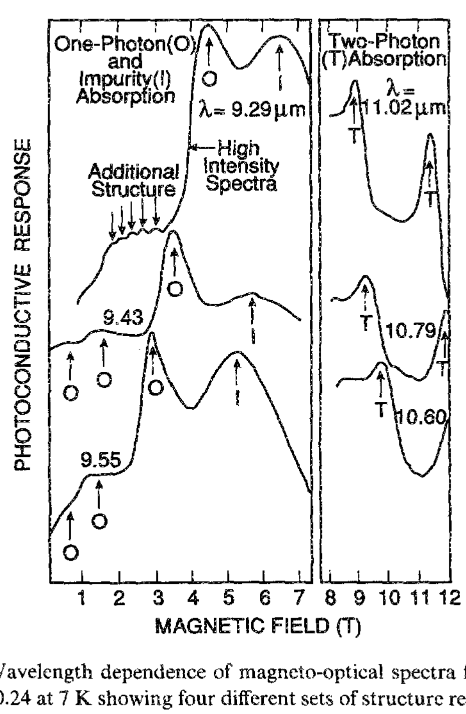

FIG. 1. Wavelength dependence of magneto-optical spectra for a sample with $x \approx 0.24$ at 7 K showing four different sets of structure related to one-photon absorption (O), two-photon absorption (T), impurity absorption (I), and the additional high-intensity structure, which is the subject of this paper. The spectra for $\lambda = 9.29\ \mu m$ have been obtained at much higher laser intensities. Boxcar averaging techniques have been used.

Figure 2 shows that at low intensities only a one-photon absorption structure is present, while at higher intensities a series of structures develops on the low-field (or high-energy) side of the dominant one-photon peak at ≈ 4.2 T. The magnetic field positions of this new, high-intensity structure are independent of wavelength, as shown in Fig. 3. In the higher field regions of these spectra, one sees one-photon and impurity absorption structure which clearly has a dependence on wavelength or photon energy. In order to interpret better this wavelength-independent structure, ac magnetic-field modulation and lock-in amplifier techniques were employed to increase the resolution of the oscillations. An example of the improved resolution obtainable is seen in Fig. 4 where the second derivative of the PC response is plotted as a function of magnetic field.

Another sample with $x \approx 0.22$ exhibits similar wavelength-independent structure in the PC response, as shown in Fig. 5. It is strikingly clear that the two high-field peaks are much larger than the rest of the lower field series. Since the band gap energy is 95 meV for this sample, the largest one-photon peak has shifted out of our measurable field range; thus all of the structure can be attributed to the new mechanism. Figure 6 shows the second derivative of the PC

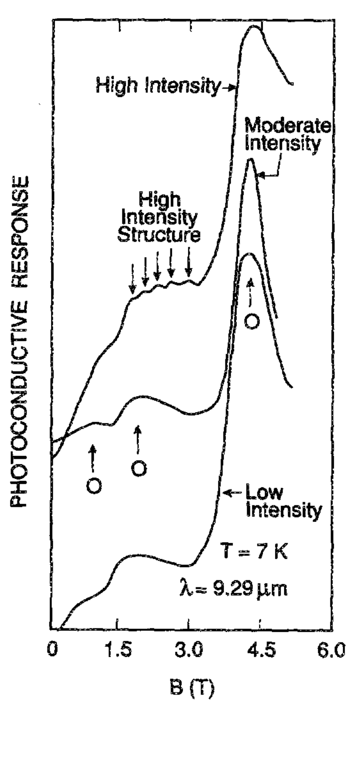

FIG. 2. Intensity dependence of the one-photon and the high-intensity structure for a sample with $x \approx 0.24$ using boxcar averager techniques.

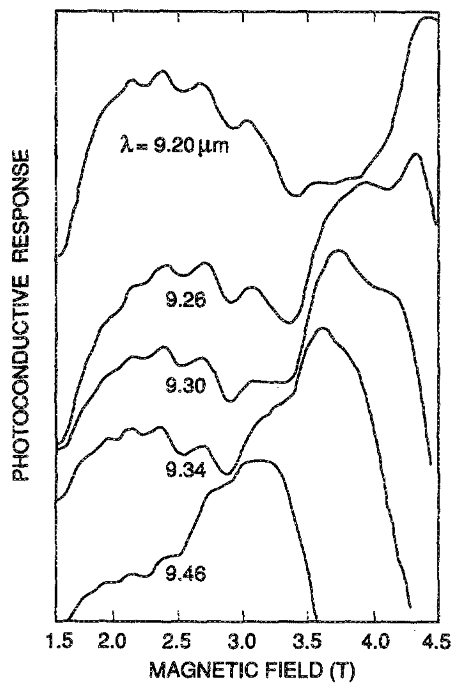

FIG. 3. Wavelength dependence of the high-intensity structure showing the independence of the peak positions on photon energy using boxcar averager techniques.

response using the ac magnetic field and lock-in amplifier technique. The sensitivity of the derivative method is clearly superior at low fields, with many more oscillations observable below 2 T (2 T is the limit of observability of the structure seen in Fig. 5). Figure 6 clearly shows two dominant sets of structure: long period structure at lower fields and higher frequency structure above 1.5 T. The complexity of

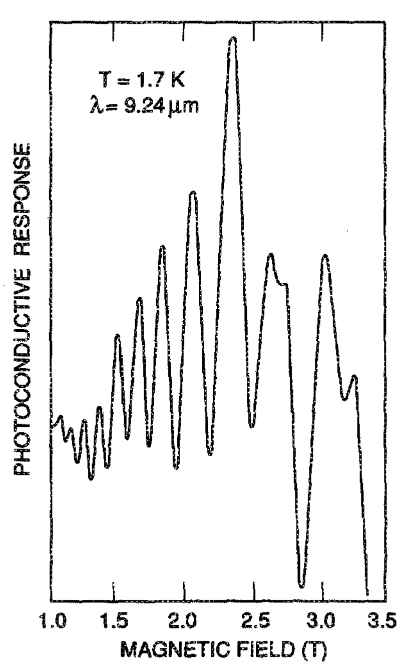

FIG. 4. High-resolution data obtained by using, in addition, ac magnetic field modulation and lock-in amplifier techniques. The lock-in amplifier output plotted on the y-axis represents the second derivative of the photoconductive response vs magnetic field.

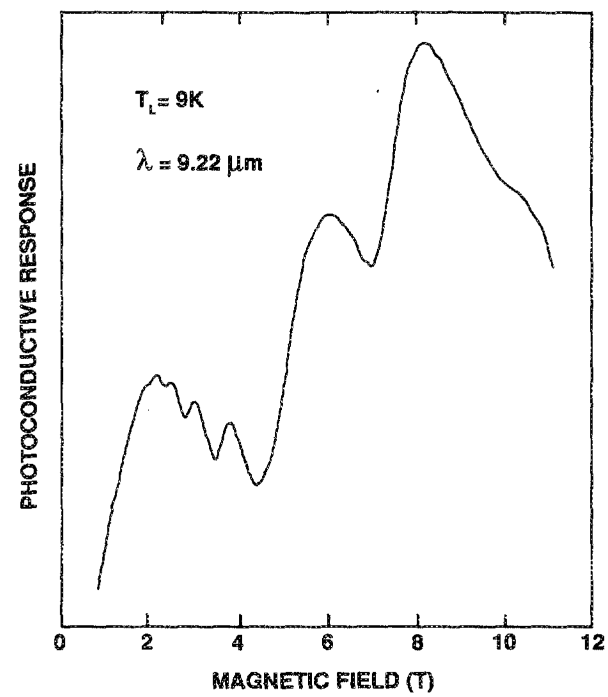

FIG. 5. Photoconductive response vs magnetic field showing the high-intensity structure obtained for a sample with $x \approx 0.22$ by using boxcar averager techniques.

the data at high fields also indicates another possible set of structure.

The resonance conditions that lead to the oscillations in the photoconductive response are pictured in Fig. 7. Electrons are photoexcited across the energy gap and subsequently high into the conduction band by absorption of a second photon of energy $\hbar\omega$. Note that if the photon energy is less than the separation between the highest Landau level in the valence band and the lowest in the conduction band,

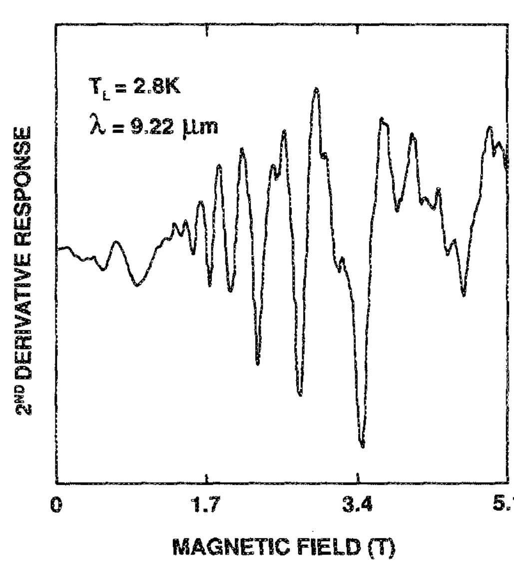

FIG. 6. High-resolution data obtained by using, in addition, ac magnetic field modulation and lock-in amplifier techniques. This second derivative behavior shows important structure at low fields and other structure at high fields that cannot be seen with the boxcar technique.

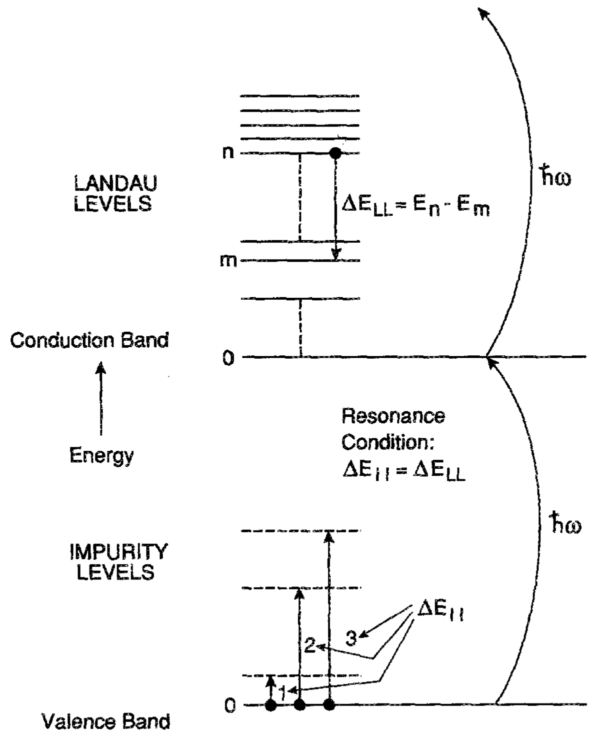

FIG. 7. A schematic of the electronic transitions that lead to the observed resonances. ΔE_{LL} is the energy difference between the initial and final conduction-band Landau-level energies. ΔE_{II} is the difference between the energy of the impurity level and the highest valence-band Landau level. Resonances occur when $\Delta E_{LL} = \Delta E_{II}$. Photons of energy $\hbar\omega$ excite electrons across the gap and subsequently well into the conduction band.

the sample is observed to be almost transparent and the signal goes to zero. For a resonance the transition energies ΔE_{LL} between conduction-band Landau levels must equal the transition energies ΔE_{II} between the highest valence-band Landau level and an impurity level in the gap. The arrows indicate the electron transitions from their initial to final states. Landau levels that are more than a photon energy above the lowest conduction-band Landau level are not populated and therefore do not contribute. An alternative possibility by which the electrons can be promoted high into the conduction band is through Auger processes. This would not affect the interpretation of our data.

A computer code was written to determine the transitions that correspond to the observed peaks. The series of conduction-band Landau levels and the upper valence-band Landau level were computed for the energy gaps of the two samples, 95 and 122 meV. A modified Pidgeon–Brown band model[5] was used with Weiler's set of band parameters[5]: $E_p = 19$ eV, $\Delta = 1$ eV, $\gamma_1 = 3.3$, $\gamma_2 = 0.1$, $\gamma_3 = 0.9$, $\kappa = -0.8$, $F = -0.8$, $q = 0.0$, and $N_1 = 0.0$. The sample orientation was assumed to be $\langle 111 \rangle$, and no exciton corrections were made since the structure is introduced not by the absorption process but by the relaxation process. Within the precision of our measurements, anisotropy effects are not expected to be important. The energy versus magnetic field dependence of the Landau levels is fitted with a parabolic spline. Note that the small gap of mercury cadmium telluride leads to a strongly nonparabolic band and thus to a nonlinear dependence of Landau level energies on magnetic field. A value is then given as input to the code for the energy of the impurity level above the valence band at zero magnetic field. The code searches for magnetic fields that satisfy the resonance condition. Successive values for the impurity-level energy are used until agreement is obtained between theory and experiment. The code furnishes as output the values of the magnetic fields, Landau level numbers for the transitions, and the actual energies of the impurity level above the upper valence-band Landau level. It is assumed that the impurity/defect level does not shift with magnetic field.

The results for the two samples are given in Tables I and II. Table I gives the values for the experimental and theoretical magnetic fields, $B^{\exp}$ and B^{th}, respectively, in tesla, the Landau level numbers for the transitions, and the resonance energies in milli electron volts for sample I with $x \simeq 0.22$ and a gap of 95 meV. All of the resonances correspond to the series of Landau levels with spin state "a." This result implies that those states are preferentially pumped by the radiation and that spin is conserved as well in the downward transitions involving impact ionization. The data would show further splittings than are observed if the "b" spin state Landau levels were involved. Three distinct impurity levels were extracted from the data. The first is at very low field and corresponds to an impurity level of 15 meV at zero field. Only transitions to the lowest Landau level were observed ($1 \to 0$, $2 \to 0$, $3 \to 0$, $4 \to 0$). Those corresponding to the upper-level transitions were either too "smeared" at these low fields or quenched by phonon-assisted transitions between the levels. This energy corresponds to a commonly observed shallow acceptor level.[3] An alternate explanation would be that the low field structure may be associated with an impurity-shifted magnetophonon effect where the donor is nearly degenerate with the lowest conduction-band Landau level.

TABLE I. Experimental $B^{\exp}$ and theoretical B^{th} magnetic field positions for the peaks in the photoconductive response, along with the conduction band Landau level numbers associated with the transitions and the impact ionization energies E_{II} between the upper valence band Landau level and the impurity/defect level for the sample with $x \simeq 0.22$.

$B^{\exp}$(T)	B^{th}(T)	Transitions	E_{II} (meV)
0.263	0.276	$4 \to 0$	15.0
0.357	0.372	$3 \to 0$	15.1
0.584	0.568	$2 \to 0$	15.1
1.20	1.19	$1 \to 0$	15.2
1.25	1.23	$10 \to 4$, $7 \to 2$	45.2
1.38	1.38	$8 \to 3$, $5 \to 1$	45.2
1.54	1.50	$3 \to 0$	45.2
1.75	1.68	$9 \to 4$, $6 \to 2$	45.2
2.01	2.00	$7 \to 3$, $4 \to 1$	45.3
2.40	2.35	$8 \to 4$, $2 \to 0$	45.3
2.48	2.55	$5 \to 2$	45.4
2.85	2.95	$6 \to 2$, $4 \to 1$	59.4
3.13	3.13	$6 \to 3$	45.4
3.61	3.54	$3 \to 1$	45.5
3.78	3.77	$5 \to 2$, $2 \to 0$	59.5
4.83	4.83	$4 \to 2$	45.7
6.01	5.75	$3 \to 1$	59.8
8.07	8.25	$1 \to 0$	60.0

TABLE II. Experimental B^{exp} and theoretical B^{th} magnetic field positions for the peaks in the photoconductive response, along with the conduction band Landau level numbers associated with the transitions and the impact ionization energies E_{II} between the upper valence band Landau level and the impurity/defect level for the sample with $x \approx 0.24$.

B^{exp}(T)	B^{th}(T)	Transitions	E_{II} (meV)
1.12	1.18	9→1, 7→0	61.2
1.21	1.19	10→2	61.2
1.28	1.26	8→1, 6→0	61.2
1.39	1.41	9→2	61.2
1.51	1.52	7→1, 5→0	61.2
1.64	1.69	10→3, 8→2	61.2
1.81	1.87	6→1	61.3
2.02	1.98	9→3, 4→0	61.3
2.27	2.24	10→4, 7→2	61.3
2.55	2.54	8→3, 5→1	61.3
2.65	2.65	3→0	61.4
2.91	⋯	⋯	⋯
3.11	3.03	6→2	61.4

However, the determination of 15 meV ± 0.5 meV for this energy seems to preclude this assignment since the LO phonon energy is approximately 17 meV.

The second level identified is at 45 meV, which is near the middle of the gap. These mid-gap levels have been seen many times before (see review of impurity levels in Ref. 3). A third level was found at 59 meV above the valence band (or at 0.62 E_g), which is closer to the conduction band. This level is the origin of the four high-field peaks in the data of Fig. 5. The lower-field peaks correspond to the 45-meV level. Some of these peaks also appear in the doubly differentiated signal given in Fig. 6. It is interesting to examine the structure of the data given in Fig. 6. The structure at low field tends to grow in amplitude and "stretch" with increasing field. This behavior is also seen in the structure for the other two sets of data. In fact, the calculations of the peak positions bear this out by showing how the peaks should become progressively broader and less frequent with increasing field. There is an interference between the second and third set of peaks in the vicinity of 3–4 T, and this interference is a sign that two different sets of resonances occur.

The data given in Table II are for the sample with $x \approx 0.24$ and $E_g = 122$ meV. Only one set of resonances was observed with an impurity-level energy of 61 meV above the valence band at zero field. This energy is at the middle of the gap. All of the peaks have been accounted for except one at 2.91 T. Presumably, this peak is associated with an impurity level closer to the conduction band as is true for the third set of Table I. However, the data do not go to a sufficiently high field to obtain a value for this third level. Likewise, the data did not extend to a field low enough to see the peaks corresponding to level one of Table I. This method has found mid-gap levels in both samples which are expected to exist in these materials. This result lends support to the validity of our interpretations.

Recent magneto-optical spectroscopy work on a *p*-type HgCdTe sample with $x = 0.216$ and $E_g = 91$ meV found deep levels at 0.49 and 0.66 E_g above the valence band.[6] This is in good agreement with our 0.47 and 0.62 E_g determination for the $x \approx 0.22$ sample, and 0.5 E_g for the $x \approx 0.24$ sample.

Finally, we point out that the magneto-impurity effect involving donor levels can be ruled out as an explanation for the origin of the observed high-intensity structure reported in this paper. Because of the extremely light mass of the electrons, the energy separation calculated using this model between ground and excited states of a donor and the observed periodicities gives values comparable to the energy gap of the samples.

IV. CONCLUSIONS

We have investigated structure in the photoconductive response of *n*-type $Hg_{1-x}Cd_xTe$ samples with $x \approx 0.22$ ($E_g = 95$ meV) and 0.24 ($E_g = 122$ meV) at 2–10 K in the presence of a magnetic field and under intense laser illumination. Oscillatory behavior as a function of magnetic field was observed in the photoconductive signal. The second derivative of this signal showed even more oscillations that were too small to be observed in the primary signal. The peaks of these oscillations were shown to correspond to resonances associated with Landau-level transitions. When the energy difference between any two conduction-band Landau levels is equal to the energy needed to impact-ionize a valence electron from the highest valence-band Landau level into a trap, there is a peak in the data. Similar resonances have been seen before, associated with impact ionization of shallow impurities from ground to excited states.[1] However, this is the first time that such an effect has been seen for impact ionization into deep traps. We have seen resonances in the sample with $x \approx 0.22$ that correspond to impact ionization from the highest valence-band Landau level into the shallow acceptor at about 15 meV, and into two deep levels, one at 45 meV and the other at 59 meV above the valence-band edge at zero field. We have also seen a level at 61 meV in the sample with $x \approx 0.24$. These mid-gap levels have been seen before in similar samples and support these results.[3] This technique should be useful for the investigation of deep-level impurities in narrow-gap semiconductors which are difficult to measure by conventional methods.

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[1] See, for example, the review of the magneto-impurity effect, L. Eaves and J. C. Portal, J. Phys. C **12**, 2809 (1979).
[2] D. G. Seiler, C. L. Littler, M. R. Loloee, and S. A. Milazzo, J. Vac. Sci. Technol. A **7**, 370 (1989).
[3] C. L. Littler, D. G. Seiler, and M. R. Loloee, J. Vac. Sci. Technol. A **8**, 1133 (1990).
[4] See the discussions presented in Refs. 2 and 3 above.
[5] M. H. Weiler, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1981), Vol. 16, p. 119.
[6] Z. Kucera, P. Hlidek, P. Hoschl, V. Koubbele, V. Prosser, and M. Zvara, Phys. Status Solidi B **158**, K173 (1990).