

residual resistivity that is consistent with experiment. We must note, however, that it is by no means necessary that any single crystal be characterized by a single \bar{Q} direction throughout. It is possible for a \bar{Q} -domain structure to exist. This \bar{Q} -domain structure, in fact, provides an explanation for the sample dependence of the anisotropies seen in induced-torque experiments.^{1,2} Since the torque anisotropies in sample *K*-10 of Holroyd and Datars are larger by an order of magnitude than those in other samples, we conjecture that it was probably the only single- \bar{Q} sample that has ever been studied.

A difficulty for the CDW model in potassium stems from the results of the de Haas-van Alphen (dHvA) experiments.³ However, it is not clear what effect a multiple \bar{Q} -domain structure would have on the results of these experiments.¹³ Unfortunately, dHvA experiments have never been done on samples that are known to exhibit the large torque anisotropies shown in Figs. 1 and 2. Therefore, with induced-torque measurements as a tool for characterizing samples, it would be extremely interesting to perform dHvA experiments on a sample that exhibits the large torque anisotropies discussed here.

A CDW structure will lead to weak diffraction satellites. Phase excitations⁹ may reduce their intensity in *K* by several orders of magnitude. A search for these satellites at 10^{-7} of the (110) in-

tensity level should be attempted.

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Large-Lattice-Relaxation Model for Persistent Photoconductivity in Compound Semiconductors

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A new model, based on an extremely strong coupling between the electronic and vibrational systems of certain defect centers, is proposed to explain the phenomenon of persistent photoconductivity observed in some compound semiconductors. The model is supported by data on donor-related defects in *n*-type $\text{Al}_x\text{Ga}_{1-x}\text{As}$ which exhibit the features characteristic of this effect: a very large Stokes shift (thermal depth, ~ 0.1 eV; optical depth, ~ 1.2 eV); and a very small ($< 10^{-30}$ cm²), thermally activated, electron-capture cross section at temperatures below 77 K.

Many compound semiconductors exhibit persistent impurity photoconductivity at temperatures below about 77 K. This very striking, and puzzling, effect is characterized by a large photoconductivity which persists for hours, or even days, after the optical excitation is removed. It can only be quenched by heating the sample above some characteristic temperature. Such effects

have been observed in $\text{Al}_x\text{Ga}_{1-x}\text{As}$,¹ $\text{GaAs}_{1-x}\text{P}_x$,² $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$,³ CdTe ,⁴⁻⁶ GaSb ,⁷ and CdS .⁸ The long persistence time implies that the capture cross section for the photoexcited carriers is less than 10^{-30} cm². This is *six orders of magnitude* smaller than the smallest capture cross section of any well-characterized attractive, repulsive, or neutral center in Si, Ge, or III-V semiconductors.⁹⁻¹¹

In addition, the capture process at these photoconductivity centers is thermally activated at temperatures below ~ 100 K with large activation energies (0.15 eV in GaSb,⁷ 0.18 eV in $\text{Al}_x\text{Ga}_{1-x}\text{As}$,¹ and 0.5 eV in CdTe⁶ and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ³). No well-characterized center shows such strongly activated behavior at such low temperatures.^{9,11}

Another very striking property of the centers responsible for persistent photoconductivity is an unusually large Stokes shift. As we will discuss later, the defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ have a thermal depth of about 0.1 eV while the transition which excites the photoconductivity has a threshold at about 0.6 eV and a maximum photoresponse at about 1.2 eV. MacMillan⁵ observed a similar effect in CdTe:Cl with a thermal level 0.05 eV above the Γ conduction-band minimum and an optical threshold of 0.8 eV with a 1.4-eV maximum. Burkey *et al.*,³ have shown that the defects in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ have thermal depths between -0.05 and 0.28 eV with an optical threshold of 0.9 eV and a maximum at about 1.4 eV. Furthermore, this Stokes shift is also manifested in the inability to quench the photoconducting state optically^{1,8}; i.e., the transition from the valence band to the empty defect level is shifted to an energy larger than the semiconductor band gap.

In order to study this class of defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ under more controlled conditions than those possible with photoconductivity, we have used various forms of junction-capacitance spectroscopy.^{12,13} These techniques allow a straightforward determination of the thermal emission and capture properties of these defects as well as their concentration and optical line shape.

Figure 1 shows representative data for the electron thermal capture and emission rates as a function of temperature in a typical sample. The processes have a markedly nonexponential time dependence so that the assignment of a rate is somewhat arbitrary. In addition, the rates varied by as much as a factor of 5 among samples from various crystals but showed no systematic trends with alloy composition. This and the ambiguities inherent in the nonexponential behavior may account for the slight difference between our data and those of Nelson,¹ also shown in Fig. 1. The concentration of these defects was roughly proportional to the donor concentration (Te or Se, $N_D - N_A = 5 \times 10^{16} - 2 \times 10^{18} \text{ cm}^{-3}$) but varied somewhat from sample to sample, suggesting that the defects are some sort of a complex of a donor atom with a native defect or ubiquitous impurity.

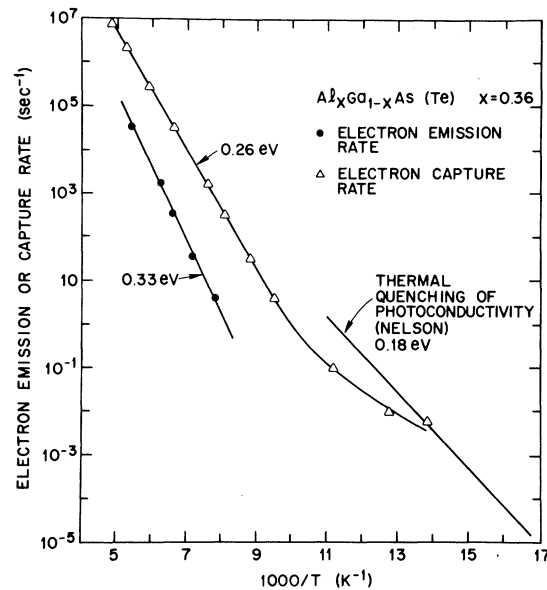


FIG. 1. Electron-emission and -capture rates vs inverse temperature for a typical sample of $\text{Al}_x\text{Ga}_{1-x}\text{As}(\text{Te})$. The photoconductivity data are taken from Ref. 1.

It is noteworthy that the defect concentration may be nearly as large as the net donor concentration in some samples. Nelson¹ has shown that this defect is a donor; thus it is often the *dominant* donor responsible for the room-temperature conductivity of $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

In spite of the above-mentioned variations, the average defect properties are well enough defined in a wide range of crystals with various alloy compositions ($0.22 < x < 0.8$) and doping for development of a model which is capable of explaining the overall features of this class of defects. The configurational-coordinate (cc) diagram for our model is shown in Fig. 2. We note that this is not a usual cc diagram showing relaxation associated with an intra-atomic transition. We wish to consider the more general case as discussed by Henry and Lang¹¹ of lattice relaxation associated with a free-to-bound transition. Thus, in Fig. 2, curves *V* and *C* correspond to the total system energy of an unoccupied defect with a delocalized electron in either the valence or conduction band, respectively. Vibrations of the defect coordinate *Q* have no effect on the delocalized electrons but increase the energy of the system. Thus these curves do *not* correspond to vibrations of the bands, but rather of the unoccupied defect. Curve *D*, on the other hand, corresponds to the vibrations of an occupied defect. For well-known

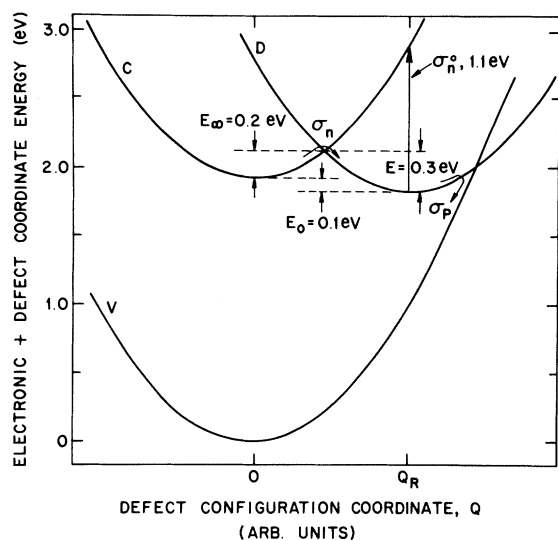


FIG. 2. Configuration-coordinate model for the donor-defect center in $\text{Al}_x\text{Ga}_{1-x}\text{As}(\text{Te})$.

defects,¹¹ curve D would be only slightly shifted from $Q=0$ and the minimum of curve C would be nested *inside* curve D , i.e., the C - D crossing point would be to the left of $Q=0$. In this *small-relaxation limit*, multiphonon (MP) carrier capture occurs at low temperatures by a tunneling transition due to an overlap of the vibronic states associated with the unoccupied (C) and occupied defect (D). For such tunneling transitions the capture cross sections are only weakly dependent on temperature below about 150 K and are typically greater than about 10^{-21} cm^2 .¹¹ Figure 2, on the other hand, corresponds to the *large-relaxation limit* where the minimum of curve C does not overlap with any vibronic states of curve D . Thus MP electron capture can *only* occur by thermal excitation of the system to near the C - D crossing point. Hence the capture cross section is thermally activated even at low temperatures and can be many orders of magnitude smaller than is typical of the small-relaxation tunneling limit.

The physical significance of the large-relaxation limit is that the defect level is above the conduction-band minimum in the configuration symbolized by $Q=0$, but when energy is supplied to distort the local environment of the defect to $Q=Q_R$ the level drops deep into the gap; i.e., there is a strong coupling between the electronic and vibrational systems of the defect analogous to that often found in molecules. The *net* energy E_0 gained in such a process may be small, however; for example, E_0 for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ (such as would

be measured by a Hall experiment) is only 0.1 eV (cf. Fig. 2). Indeed, this energy could even be *negative* if the conduction-band minimum chosen for curve C were below the equilibrium energy of the occupied defect level, such as at Γ in $\text{CdTe}:\text{Cl}$ (Refs. 3, 5, and 6) or $\text{Al}_x\text{Ga}_{1-x}\text{As}:\text{Te}$ ($x < 0.35$). Since optical transitions can occur only at constant Q , such a defect will appear to be very deep optically; e.g., in Fig. 2 the optical cross section σ_n^0 for exciting an electron from the defect to the conduction band has a maximum at about 1.1 eV.

The very simple cc diagram in Fig. 2 [see Eq. (7) of Ref. 11 for the general analytical form], which makes no effort to include the nonlinear effects which must be present, nonetheless gives remarkable insight into the basic physics of persistent-photoconductivity centers. In particular, for the case of Te-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ the quantitative agreement is surprisingly good. When the straightforward experimental corrections¹⁴ are applied to the data in Fig. 1 we obtain the thermal barrier to electron capture $E_\infty \sim 0.2$ eV and the thermal barrier to electron emission $E \sim 0.3$ eV. The net binding energy $E_0 \sim 0.1$ eV obtained from the difference of E and E_∞ according to the procedure of Ref. 14 agrees very well with the direct measurement of $E_0 \sim 0.1$ eV from Hall measurements.¹ Since these thermal data completely determine our simple cc diagram, it is remarkable that the predicted photoexcitation maximum of 1.1 eV is so close to the experimental value of 1.2 eV.

A diagram such as Fig. 2 thus readily explains the two dominant features of persistent photoconductivity: the extremely small, thermally activated, electron-capture cross section at low temperatures (≈ 100 K), and the very large Stokes shift. The lack of an optical quenching path is also apparent in Fig. 2; i.e., the defect state at $Q=0$ is far up in the conduction band and hence cannot be filled by sub-band-gap light. Thus we believe that the very simple model expressed in Fig. 2 contains the physical essence of this class of defects which is apparently present in a wide variety of compound semiconductors.

Three other models have been previously proposed to explain this phenomenon. However, we feel that, unlike our model, none of them can adequately account for *all* of the characteristics of the effect. The first²⁻⁴ supposes that the defects in question are double acceptors and hence present a Coulomb repulsive barrier to the recapture of photoexcited electrons. We believe this model is inadequate, however, since normal Coulomb repulsive centers^{9,10} have capture cross sections

which are neither small enough nor temperature dependent enough to explain the behavior of the very long persistence times typically observed. In addition, the double-acceptor model is unable to account for the large Stokes shifts. This is not to say that the defects may *not* be single or double acceptors; indeed, the defects in $\text{Ga}_{1-x}\text{As}_x\text{P}$,² $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$,³ and CdTe ⁴ have all been shown to be acceptors by an increase in mobility after photoexcitation. In $\text{Al}_x\text{Ga}_{1-x}\text{As}$, on the other hand, the defects have been shown to be donors by virtue of a decrease in mobility after excitation.¹ Thus we feel that the donor or acceptor nature of the defects is not a determining factor for persistent photoconductivity observed at 50 K and above. The double-acceptor effect may, however, be important at very low temperatures. For example, in closely compensated Zn-doped Ge a weakly persistent (<200 sec) photoconductive effect has been observed for temperatures below 30 K.¹⁰ But, unlike the effects which we are considering, this double-acceptor effect could be optically quenched.

A second model^{6,7} supposes that persistent photoconductivity is due to a band-structure effect in which electrons at the X or L points of the Brillouin zone have a much higher capture cross section at the defect than do electrons at the zone-center Γ point. Thus electrons which are photoexcited from the defect are rapidly thermalized into the conduction-band minimum at Γ where they are strongly prohibited from being recaptured at the defect. We believe that this model is also inadequate to explain the photoconductivity results. This is because our experimental results and those of Nelson¹ on the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ system as well as those of Craford *et al.*² on $\text{GaAs}_{1-x}\text{P}_x$ and Burkey *et al.*³ on $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ show that the capture properties of the defects involved are relatively insensitive to changes in alloy composition. Such changes, however, give rise to very large changes in the band structure, so that it is not likely that a band-structure model alone could be totally correct. We do not, however, rule out the possibility that the defect levels may be associated primarily with the non- Γ conduction-band minima and possess some of the features postulated by this model. In fact, there is very good evidence from hydrostatic-pressure experiments that such non- Γ levels do indeed exist.⁶ As we will discuss below, the defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ also behave as non- Γ levels and thus are resonant states at Γ in the direct-gap composition range.

A third model has been proposed for the case of CdS which postulates three different levels to explain the effects.⁸ While such a complicated model may be necessary to explain the behavior of systems with many defects and impurities, we believe that our data on $\text{Al}_x\text{Ga}_{1-x}\text{As}$ crystals of well-controlled, uniform doping suggest that the essential features of persistent photoconductivity may be explained by a much simpler model.

Finally, we wish to comment briefly on another aspect of the donor-defect center in $\text{Al}_x\text{Ga}_{1-x}\text{As}:\text{Te}$ which may be related to, but is not the principal cause of, the photoconductivity effects discussed above. Namely, the state appears to be strongly associated with the conduction-band minima at X and L so that for $x < 0.35$ it can exist relatively unperturbed as a *resonant state* in the low-density-of-states conduction-band continuum at Γ , i.e., E_0 is negative if measured from Γ . This resonant-state behavior causes the defect capacitance signal to fall exponentially by over three orders of magnitude from $x = 0.35$ to $x = 0.22$ due to incomplete filling of the level when it is above the Fermi level at the Γ minimum. Applied stress also changes the signal strength in this region by an amount consistent with the known deformation potentials. Despite the fact that the level is clearly far above the Fermi level, and hence resonant with the Γ density of states, we see only small changes in the thermal emission and capture properties of the center in this direct-gap composition region.

The complex nature and large relaxation of this center is suggestive of a rather low symmetry. Such a center would most likely be formed predominantly from band states away from the symmetric zone center and hence would have very small coupling to Γ . This may account for the localized resonant state which we observe. In general, it may be that the large relaxation and non- Γ characteristics of this class of defects are intimately related in just such a way. We believe, however, that the optical and capture properties of these defects, and hence persistent photoconductivity, are dominated by the effects of lattice relaxation.

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Electronic Structure of the Thorium Hydrides ThH₂ and Th₄H₁₅

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Photoelectron spectroscopy using synchrotron radiation has been used to study the electronic structure of single-phase stoichiometric ThH₂ and Th₄H₁₅. Th-derived conduction bands are observed together with lower-lying hybridized bonding bands. For Th₄H₁₅, a narrow *d*-like conduction band (~0.6-eV full width at half-maximum) separated from other bands by a 2-eV band gap is seen. Energy-dependent cross-section measurements for the various bands have been used to determine hybridization and angular momentum character.

In this Letter, we present the first photoelectron spectroscopy (PES) study of the electronic structure of well-characterized, single-phase metal hydrides. The hydrides of thorium, ThH₂ and Th₄H₁₅, were chosen since they have quite different metal hydride stoichiometries. ThH₂ is a fairly representative CaF₂-structured metal dihydride (complicated somewhat by relativistic effects in Th with a slightly distorted fcc structure and 5*f* electronic states), and Th₄H₁₅ is a strong superconductor ($T_c \approx 9$ K) with one of the highest hydrogen-to-metal ratios of any metal hydride. We have sought to observe bandlike 5*f* states in Th₄H₁₅ which, it has been suggested,¹ are responsible for the high superconducting transition temperature in Th₄H₁₅. Our results show no conclu-

sive evidence for the presence of such 5*f* states in Th₄H₁₅. We do find a very narrow occupied conduction band (~1 eV wide) at E_F which is separated by a large ~2-eV "band gap" from the bonding states. By examining both hydrides under similar experimental conditions, we have determined the sensitivity to the hydrogen stoichiometry of the bonding bands and the conduction bands near the Fermi energy, E_F , and, by examination of the relatively shallow 6*p* core levels of thorium, have determined shifts in E_F corresponding to changes in the hydrogen content. (By conduction bands, we mean the bands near E_F which are mainly thorium-derived and have not mixed strongly with hydrogen states; the hybridized Th-H covalent bonding bands lie beneath the met-