In the general case one may argue that there will be no degeneracy (except accidental) if there is no symmetry in the problem. We are vitally concerned, however, with the order of magnitude of the splitting at near misses, because a splitting greater than the order of 1 cm^{-1} might be incompatible with the angular width of the anomalous anisotropy in the experiment of Dillon and Nielsen. This limit is to be compared with pure crystal field splittings presumed for Tb^{+++} to be of the order of 10 cm^{-1} between levels. The magnitude of the repulsive splitting may be reduced for high J values. Consider again the Hamiltonian (B.2), now for $J=S=6$. Crossovers occur for H parallel to the axis and the degeneracies are lifted when a perpendicular field component is applied. The matrix elements of S_xH_x between the crossing levels may be considerably reduced below the example for $S=1$. If two levels having $\Delta m \neq \pm 1$ cross for H parallel to the axis, then a perpendicular component H_x will not split the crossing in second order of perturbation theory. To take a fairly extreme case, consider a crossing between the levels $m_J=J$ and $m_J=0$, for $J=6$. If we rotate axes to $\theta=30°$ the mixture of the amplitude of $|0\rangle$ into the state originally $|6\rangle$ is about 0.01, using the Wigner rotation coefficients. The amplitude of $|1\rangle$ will be of the same order, so that for this angle the splitting at a crossover is of the order $0.01H$, or ~ 0.1 cm^{-1} in a rare earth iron garnet.

One would not expect examples as favorable as this—that is, with as small splittings as 0.1 cm^{-1}, to arise very frequently. We should remember, however, that an anisotropy peak which does not increase or sharpen below 4°K only requires a splitting of the order of 3 cm^{-1}, and such a splitting may not be a rare event.

PHYSICAL REVIEW VOLUME 117, NUMBER 3 FEBRUARY 1, 1960

Recombination and Trapping in Tellurium

J. S. Blakemore, J. D. Heaps, K. C. Nomura, and L. P. Beardsley
Honeywell Research Center, Hopkins, Minnesota

(Received August 24, 1959)

Photoconductive decay in nearly perfect Te crystals shows a lifetime of up to 50 μsec at 300°K. The temperature dependence does not support previous suggestions of radiative recombination; at temperatures below 150°K marked trapping of excess minority electrons occurs, and at higher temperatures also the results suggest the activity of levels within the gap. Probably chemical impurities behave as recombination centers, and dislocations certainly act in this capacity (lifetime is reduced to ~1 μsec when 10^6 dislocations/cm^2 are introduced).

THE semiconducting properties of tellurium have been studied for some years, but many early results suffered from the unavailability of good single crystals. Crystals of high perfection are now available,[1] and a more realistic appraisal of the properties is possible, including carrier lifetime τ_T as a function of temperature T(°K).

Moss[2] estimated $\tau_{90}\sim 400$ μsec for evaporated Te layers and concluded that τ_{300} was some 10^4 times smaller. de Carvalho[3] also reported $\tau_{300}\sim 10^{-8}$ sec from P.E.M. measurements. Redfield[4] measured $\tau_{100}\sim 20$–50 μsec using photoconductive techniques; he concluded that lifetime must be very short at 300°K since he could not detect any photoconductance there. The same author suggested[5] that direct optical recombination should be more important than Shockley-Read decay in tellurium. But since Moss[6] calculates an optical lifetime of order 30 μsec at 300°K and 300 msec at 77°K, it is evident that other processes must have controlled Redfield's tellurium. There is a better chance that optical recombination could make a significant contribution in some tellurium we have been studying, since our samples yield τ_{300} as large as 50 μsec.

Redistillation and zone refinement are helpful up to a point in increasing τ_{300} for tellurium, but the benefits of purification can only be realized if the dislocation density is kept small. A standard etch readily exposes dislocation etch pits on the $10\bar{1}0$ face[7]; these pits have an asymmetric form which suggests that the dislocations themselves may run along $10\bar{2}0$ directions. We have examined crystals with dislocation densities $N_D<10^4$ cm^{-2}, yet since tellurium deforms plastically very easily, a density of 10^6 cm^{-2} or more can be introduced under a relatively small stress (such as that involved in lapping one face, or in dropping a sample onto a table). When N_D is large enough to dominate the lifetime, $\tau_{300}\sim(1.3/$

[1] T. J. Davies, J. Appl. Phys. **28**, 1217 (1957).
[2] T. S. Moss, *Photoconductivity in the Elements* (Butterworths Scientific Publications, London, 1952), pp. 208–216.
[3] A. P. de Carvalho, Compt. rend. **242**, 745 (1956).
[4] D. Redfield, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge, *et al.* (John Wiley and Sons, Inc., New York, 1956), p. 566.
[5] D. Redfield, Phys. Rev. **100**, 1094 (1955).
[6] T. S. Moss, *Optical Properties of Semiconductors* (Academic Press, Inc., New York, 1959), p. 178.
[7] Preferably a slow acting etch such as hot sulfuric acid.

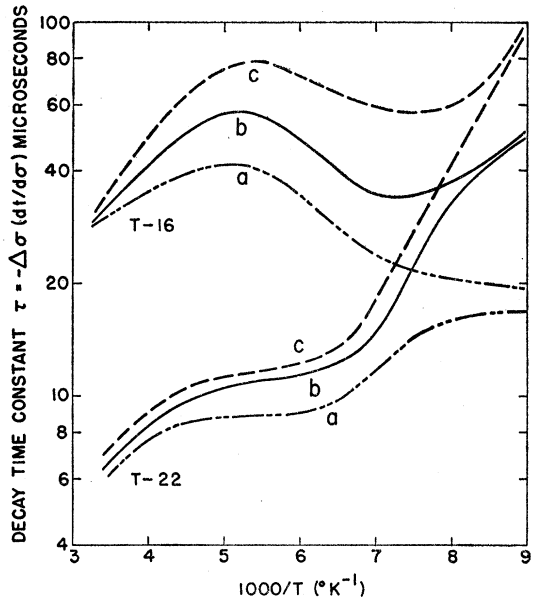

FIG. 1. For two tellurium samples, the temperature dependence of photoconductive decay time constant, as measured when $\Delta\sigma$ drops to (a) 8×10^{-3}, (b) 2×10^{-3}, (c) 5×10^{-4} ohm^{-1} cm^{-1}.

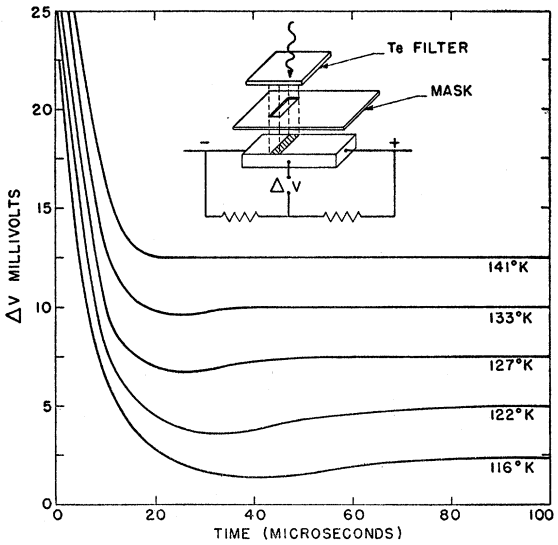

FIG. 2. For a sample with prominent trapping, the transient imbalance of a Haynes-Hornbeck bridge. Curves are separated by 2.5 mv for clarity. Drift field is the same at each temperature, and light is arranged to drive ΔV positive by 20 mv.

N_D) seconds, indicating that a dislocation corresponds with a cylinder of capture radius some 4×10^{-8} cm.

We have studied transient and steady-state photoconductivity in filaments of high perfection, usually samples with the long dimension in the 0001 direction (c axis) and with front and rear faces cleaved in $10\bar{1}0$ planes. Surface recombination asserts itself during transient decay if a sample is excited with nonpenetrating light, but the usual tests indicate that when a tellurium plate is used to filter the incident radiation, the resultant recombination and trapping are bulk phenomena.

Figure 1 illustrates for a typical pair of samples how the photoconductive decay time constant $\tau=-\Delta\sigma(dt/d\sigma)$ varies with temperature for three values of excess conductivity $\Delta\sigma$. The behavior at the higher temperatures appears to be essentially recombinative, but trapping seems to become very important below about 150°K when $\Delta\sigma\lesssim10^{-3}$ ohm^{-1} cm^{-1}. Thus at 100°K a pronounced "tail" to the decay may persist for many milliseconds; this tail can be quenched with weak ambient light. Trapping is also indicated by the difference between transient and steady-state behavior, for in measurements of dc photoconductance *versus* light intensity no sharp increase of responsivity at low levels could be found.

As a further test for traps, we used the bridge circuit of Haynes and Hornbeck[8] (Fig. 2 insert) which demonstrates the existence of a multiple trapping process. Results are shown in Fig. 2 for a specimen which appeared to have a rather low lifetime but many traps; the curves of transient imbalance for various temperatures are staggered vertically for clarity. As expected for bulk traps, the reversal of ΔV is more prominent with penetrating than with nonpenetrating light, and becomes more important when the pulsed light intensity is reduced. The curves show qualitatively the temperature dependence of "effective mobility" for excess carrier pairs (controlled by the ratio of free time to trapped time for an electron, which decreases on cooling).

It is not known yet what exact mechanisms control the *recombinative* behavior, but the results do suggest that both chemical impurities and dislocations act as recombination centers. Apart from the trap-dominated region of low temperature and low modulation, the curves of Fig. 1 are generally of the form expected from the Shockley-Read theory; thus for example in T-16 the lifetime maxima do occur at the intrinsic transition point, where $n_0\approx\frac{1}{2}p_0$. Radiative recombination may also assist at the highest temperatures for very pure samples, but this cannot be the dominant mechanism since it would require a very rapid increase in lifetime on cooling below the transition point ($\sim$180°K).

[8] J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).