PARAELECTRIC BEHAVIOR OF PbTe

R. T. Bate, D. L. Carter, and J. S. Wrobel
Texas Instruments Incorporated, Dallas, Texas 75222
(Received 11 May 1970)

Capacitance-voltage measurements on graded junction diodes of PbTe which suggest that the static dielectric constant obeys a Curie-law temperature dependence with $T_C \simeq (-79 \pm 4)$°K are reported. Evidence for nonlinear dependence of dielectric polarization on electric field is also given.

We report here the first evidence that PbTe is paraelectric; that is, we find the static dielectric constant κ_s of PbTe to be strongly temperature dependent and to be proportional to $(T-T_C)^{-1}$ (Curie law) over a large temperature range. We also report evidence for a strongly nonlinear dependence of dielectric polarization on electric field in this crystal, and suggest how these two results may lead to the resolution of some long-standing anomalies in the lead salts.

The conclusions are drawn from measurements of capacitance as a function of bias voltage on p-n junction diodes made by diffusion of donor impurities into p-type single crystals of PbTe. Diffusion times ranging from one minute to one hour were employed in the diode fabrication, resulting in junctions lying from 2 to 20 μm below the crystal surface. A detailed description of the fabrication process, which results in linearly graded junctions, will be published elsewhere. The final diode structures were "mesas" having cross-sectional areas of 6.45×10^{-4} cm^2.

The differential diode capacitance is determined using a commercial capacitance bridge over the range of dc bias in which the conductance remains within the capability of the bridge, and the ac excitation is kept below 20 mV. The capacitance is independent of frequency over the range 5-500 kHz and most of the measurements were made at 100 or 500 kHz. Data were analyzed by plotting C^{-2} and C^{-3} vs V, where C is the diode capacitance and V is the applied voltage. Below 260°K the C^{-3} vs V plots were linear (except as noted later) as is expected for linearly graded junctions in the "depletion layer," or "space charge" limit.[1] A plot of this type for a particular diode at various temperatures is shown in Fig. 1.

The most striking feature of this plot is the large change in slope from one temperature to another. The possible reasons for this change can be appreciated by examining the capacitance-voltage relation for a linearly graded junction[1] (practical units):

$$(A/C)^3 = (12/q\epsilon_0^2)[(V_b - V)/a\kappa_s^2]. \quad (1)$$

In this equation where forward bias is taken as positive, A is the cross-sectional area of the junction, κ_s is the static dielectric constant, $a = |d(N_D^i - N_A^i)/dx|$ is the fixed charge gradient at the junction, N_D^i and N_A^i are the ionized donor and acceptor densities, and V_b is the intercept of the C^{-3} vs V plot on the voltage axis. The form of Eq. (1) is correct in the depletion-layer approximation regardless of the statistical degeneracy of the carriers in the regions near the junction. The value of V_b in terms of the junction parameters will depend on this degeneracy. However, the approximate constancy of the intercepts on the voltage axis in Fig. 1 with temperature indicates that V_b is only weakly temperature dependent.

Equation (1) predicts that the slopes of the

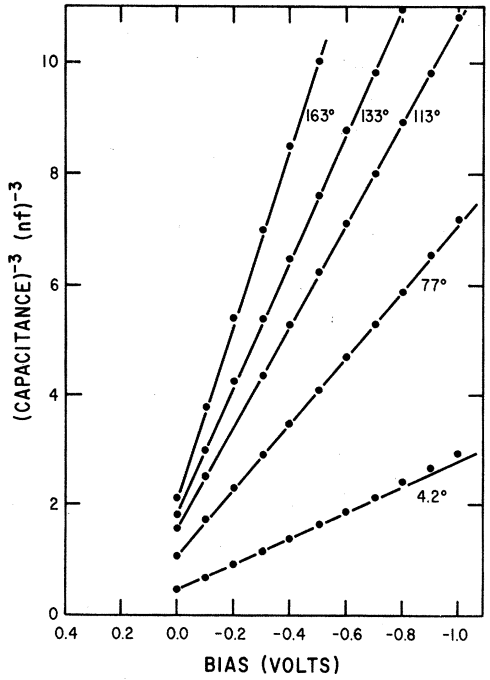

FIG. 1. Plots of capacitance^{-3} as a function of bias voltage for a diffused-junction PbTe diode at various temperatures in °K. Positive voltage corresponds to forward bias, and the junction area is 6.45×10^{-4} cm^2. These are differential capacitance values measured at 100 kHz.

lines in Fig. 1 should be proportional to $(a\kappa_s^2)^{-1}$. Now a temperature dependence of a^{-1} could arise if deionization of impurities or defects occurred in the junction as the temperature was lowered. However, this would make a^{-1} increase at low temperatures, resulting in an increased slope, which is just the opposite of the observed temperature dependence. Furthermore, changes in the extent of ionization with temperature would be expected to introduce dependences of the form $T^n\exp(\text{const}/T)$, a behavior which we shall see is not observed.

If we suppose, on the other hand, that a^{-1} is independent of temperature, then we are forced to postulate a strong temperature dependence of κ_s^{-1}. We can test for Curie-law dependence by substituting

$$\kappa_s^{-1}=\gamma(T-T_C) \tag{2}$$

into Eq. (1). The result is

$$(A/C)^{3/2}=\gamma[12(V_b-V)/aq\epsilon_0^2]^{1/2}(T-T_C). \tag{3}$$

Since V_b is nearly independent of temperature, Eq. (3) implies that a plot of $C^{-3/2}$ vs T at constant voltage will be linear if κ_s satisfies the Curie law.

Figure 2 shows a test of this type on the diode of Fig. 1 for a constant reverse bias of −1.0 V. The plot is linear within experimental error between 40 and 260°K suggesting that κ_s has the Curie-law dependence of Eq. (2) in this temperature range. Above 260° the capacitance changes rapidly with increasing temperature because of the thermal generation of carriers in the depletion layer,[1] and Eqs. (1) and (3) are no longer valid.

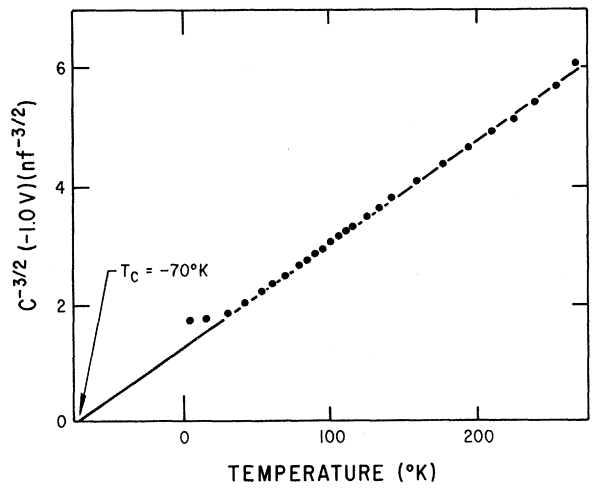

FIG. 2. Plot of capacitance$^{-3/2}$ at a fixed reverse bias of 1.0 V as a function of absolute temperature for the PbTe diode of Fig. 1. A linear behavior is expected if the static dielectric constant obeys a Curie law.

The extrapolation of the linear behavior in Fig. 2 to infinite capacitance gives the Curie temperature, $T_C=-70$°K. Combined data on three different PbTe diodes gives $T_C=(-79\pm4)$°K. Experiments on diodes made from the pseudobinary alloys $Pb_{0.95}Cd_{0.05}Te$ and $Pb_{0.83}Sn_{0.17}Te$ show behavior very similar to PbTe, and give evidence that T_C increases toward zero as the composition changes from $Pb_{1-x}Cd_xTe$ (x decreasing) to PbTe to $Pb_{1-x}Sn_xTe$ (x increasing). Data on these alloy diodes and more complete results on PbTe will be reported elsewhere.

For large reverse bias at 4.2°K, the experimental values of C^{-3} lie above the linear extrapolation (see bottom curve of Fig. 1; these measurements have been extended to 3 V reverse bias and much larger deviations are found). This can occur if the dielectric constant is electric field dependent, and is beginning to decrease at high electric field. Such an interpretation is supported by the observation that the deviations from linearity become observable at the same threshold value of dielectric polarization, $P_t \simeq C_t(V_b-V_t)/A\simeq 10^{-6}$ C/cm^2, in PbTe diodes having widely differing charge gradients. The threshold polarization for the onset of nonlinearity appears to be much higher than this in $Pb_{0.95}Cd_{0.05}Te$ and much lower in $Pb_{0.83}Sn_{0.17}Te$. The deviations from linearity on the C^{-3} vs V plots at 4.2°K are found to be proportional to $(V-V_b)^{11/3}$ within experimental error. This is the behavior expected if the polarization is related to the electric field E by[2]

$$E=4\pi\gamma(T-T_C)P+c_3P^3+c_5P^5+\cdots, \tag{4}$$

and if c_3 is negligibly small.

Capacitance measurements on abrupt junctions in PbTe which indicate very little temperature dependence of κ_s below room temperature have been reported by Kanai and Shohno.[3] This result, which appears at first to contradict ours, can be understood when one realizes that the range of dielectric polarization analyzed in their measurements lies entirely above 40×10^{-6} C/cm^2, about 40 times the threshold polarization for nonlinearity which we observe at 4.2°K. Under these conditions, the higher-power terms in Eq. (4) must dominate the first term and the temperature dependence of the first term may not be observed. The values of P covered in their experiments were, in fact, too large for the expansion (4) to

be valid, and their results seem to suggest that the relation between E and P again becomes linear and nearly temperature independent for $P > \sim 40 \times 10^{-6}$ C/cm^2. The reappearance of the linear relation between E and P for large P is, in our view, an experimental fact which is yet to be explained. Although a modification of the simplified Slater model which shows this behavior has been suggested to us, we feel it is still too speculative to present here.

Later results on diodes have been reported by Day and Macpherson.[4] However, they are difficult to evaluate because the C-V data are not presented, and the range of polarization covered cannot be determined.

With regard to the absolute value of κ_s, we are not optimistic about its determination from graded-junction measurements, because interaction of the diffusant with acceptor defects prevents a reliable determination of the charge gradient. Abrupt-junction or Schottky-barrier capacitance will work in principle, but in these cases the reduction of P below P_t requires forward biases near V_b, where the conductance is very large.

Results of experiments which can measure κ_s more or less directly under conditions of zero or negligible polarization have been reported.[5,6] However, these results, which determine κ_s in the presence of free carriers, can be mutually consistent only if κ_s increases by a factor of 10 or more between room temperature and 4.2°K. Our experiments, which determine κ_s in the absence of free carriers, do suggest a strong temperature dependence, but give only 3.8 for this ratio. A detailed study of this problem by the microwave transmission technique is now in progress in our laboratory.

A small temperature coefficient of $(5.2 \pm 2.0) \times 10^{-4}$/°K for the dielectric constant of PbTe has been inferred from neutron-diffraction experiments.[5] However, this was determined by heating the crystal above room temperature and is not necessarily inconsistent with our low-temperature results.

If the temperature-dependent polarization which we observe involves motion of the ions with respect to each other, then our results have implications for the temperature dependence and electric field dependence of the transverse-optic-mode frequency, through the Lyddane-Sachs-Teller relation.[7,2] Measurement of this frequency by techniques involving interactions near surfaces may therefore have to be performed with the surface potential under strict control. Consider, for example, the experiment of Bylander and Hass,[8] which appears to be the most reliable determination of the transverse-optical-mode frequency in PbTe at low temperatures. In these experiments, the transmission of 0.2-μm-thick films on KCl substrates was examined. However, if the potential at the free surface or at the PbTe-KCl interface were such as to produce a depletion or inversion layer in the PbTe,[9] our estimates indicate that the resultant band bending could easily extend well into the film, and that the dielectric polarization would be far beyond P_t, the threshold we observe for nonlinear behavior. (Similar arguments can be advanced with respect to the results of Watanabe.[10]) Assuming, then, that the polarization we observe in our experiments is associated with the lattice modes, we may apply the Lyddane-Sachs-Teller rule to predict that the transverse-optical mode will be shifted to considerably higher frequencies than its bulk value under these conditions. It is also noteworthy, in connection with the preceding discussion, that a strong temperature dependence of the transverse-optical-mode frequency has been observed in SnTe.[4]

Finally, we note that the anomalous increase of the carrier mobilities with decreasing temperature in PbTe and in the other lead salts at very low temperatures[11] may now find an explanation as due to ionized-impurity or defect scattering in the degenerate limit, a mobility which usually has little temperature dependence. Since this mobility is proportional to κ_s^2, an additional temperature factor $(T-T_C)^{-2}$ will be introduced into the mobility expression, and the mobility will continue to increase as the temperature is lowered, even when the electron gas is completely degenerate. As the temperature is lowered below ~20°K, we see from Fig. 2 that the Curie law is no longer obeyed and the dielectric constant becomes insensitive to temperature. This would also cause the ionized-impurity mobility to saturate just as is observed experimentally.[11]

We would like to thank R. Juarros for fabrication of the diodes and J. Adcock for technical assistance. Discussions of various aspects of this work with D. D. Buss, G. A. Antcliffe, K. W. Nill, and J. N. Walpole are also acknowledged.

[1]W. Shockley, Bell Syst. Tech. J. 28, 435 (1969); S. P. Morgan and F. M. Smits, *ibid.* 39, 1573 (1960).

[2]W. Cochran, Advan. Phys. 9, 387 (1960).

[3]Y. Kanai and K. Shohno, Jap. J. Appl. Phys. 2, 6 (1963).

[4]H. M. Day and A. C. Macpherson, Proc. IEEE, 51, 1362 (1963).
[5]W. Cochran, Phys. Lett. 13, 193 (1964); W. Cochran *et al.*, Proc. Roy. Soc., Ser. A 293, 433 (1966).
[6]Y. Sawada, E. Burstein, D. L. Carter, and L. Testardi, in *Proceedings of the Symposium on Plasma Effects in Solids* (Dunod, Paris, 1965), p. 71; S. Perkowitz, Phys. Rev. 182, 828 (1960).
[7]R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 673 (1951).
[8]E. G. Bylander and M. Hass, Solid State Commun. 4, 51 (1966).
[9]R. F. Egerton and C. Juhasz, J. Phys. D: Brit. J. Appl Phys. 2, 975 (1969).
[10]N. Watanabe, Jap. J. Appl. Phys. 3, 166 (1964).
[11]R. S. Allgaier and B. B. Houston, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962,* edited by A. C. Stickland (The Institute of Physics and The Physical Society, London, England, 1962), p. 172.

APPROXIMATE TREATMENT OF EXCITON EFFECTS IN ELECTRIC FIELD MODULATION VIA THE SLATER-KOSTER INTERACTION

J. E. Rowe and D. E. Aspnes
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 20 May 1970)

Exciton effects on electric field modulation line shapes at general critical points are treated using a Slater-Koster contact interaction to approximate the Coulomb potential. This interaction produces a mixing of one-electron line shapes similar to that calculated for an unperturbed solid. By comparison with experiment, we show that exciton effects are present in the E_1 structure of low-temperature electroreflectance data of Ge.

The one-electron approximation, which neglects the electron-hole interaction, does not predict experimentally observed optical-modulation line shapes,[1-6] and hence does not provide a means of identifying the nature of the associated transitions. This has been shown explicitly for temperature,[3] stress,[4] and wavelength modulation,[5] where spectra are related to the energy derivative of the dielectric function of the unperturbed solid. Because of this simple connection, it is possible to utilize the Slater-Koster "contact" interaction[7,8] to approximate the Coulomb interaction at higher interband critical points. The purpose of this paper is to extend the contact exciton formalism to include additional perturbations which can be described in the effective-mass approximation (EMA). This extension allows the contact exciton interaction to be included in the theory of electric field modulation and enables for the first time an approximate theoretical treatment of excitonic effects at general critical points in electroreflectance. Predicted line shapes are found to be in good agreement with low-temperature electroreflectance spectra of M_1 critical points in Ge.[9]

In the EMA,[10] the dielectric function can be written in terms of either the relative coordinate excitation energies E_α as

$$\epsilon = \frac{Q}{\pi\omega^2}\sum_\alpha \frac{1}{E_\alpha - z}, \tag{1}$$

or a resolvent (lattice Green's function) G_0 as

$$\epsilon = \frac{Q}{\pi\omega^2}\lim_{\vec{R}_j,\vec{R}_{j'}\to 0}\langle \vec{R}_{j'}|G_0|\vec{R}_j\rangle, \tag{2}$$

where $G_0 = (H_0 - z)^{-1}$, $z = \hbar\omega + i\Gamma$, $Q = 4\pi^2 e^2 m^{-2} \times |\hat{\epsilon}\cdot\vec{P}|^2$, and $\vec{P}$ is the interband momentum matrix element (which is assumed constant for simplicity). The state $|\vec{R}_j\rangle$ is a Wannier function centered on the lattice site $\vec{R}_j$, and $|\alpha\rangle$ is an eigenstate of the relative-coordinate Hamiltonian H_0, such that $H_0|\alpha\rangle = E_\alpha|\alpha\rangle$. In the unperturbed one-electron picture, $|\alpha\rangle$ represents an electron-hole pair state expressed in terms of Bloch functions, and the envelope function $F_\alpha(0) = \langle 0|\alpha\rangle$ connecting Eq. (1) to Eq. (2) is identically 1. One can easily generalize Eq. (2) by noting that a perturbing field (e.g., a uniform electric field) requires new pair states $|\varphi\rangle$ to diagonalize the perturbed Hamiltonian $\tilde{H}_0 = H_0 + H_1$. The corresponding envelope functions $F_\varphi(0)$ are generally not equal to unity. These may be found either by expanding the new eigenstates $|\varphi\rangle$ in terms of the Wannier functions $|\vec{R}_j\rangle$, or by solving the EMA Schroedinger equation for them directly.[11]

We now consider in addition to H_1 a Slater-Koster contact potential V defined as

$$\langle \vec{R}_j|V|\vec{R}_{j'}\rangle = \tilde{g}\delta_{\vec{R}_j,0}\delta_{R_{j'},0}. \tag{3}$$

Following previous treatments[7,8] of the unperturbed Hamiltonian, the resolvent operator $\tilde{G}$ in-