lattice (or the position of the anion in the Periodic Table), the spin-orbit interaction is relatively small ($\Delta_{so}\sim 11$ meV). The "normal" ordering of the spin-orbit split components emphasizes the unique nature[20] of the valence band in ZnO and its apparent dependence upon the energy of the Zn *d* bands. Although there is some evidence for further fine structure in the reflectance, its analysis, which should not change the basic conclusions reached here, must await the availability of even better-quality materials.

We have identified weak structure in the luminescence as due to the decay of a free exciton with the simultaneous creation of a photon and one or two LO phonons. The dominant emission peak at 3.467 ±0.001 eV is confidently associated with an exciton decaying at a donor site (I_2), whereas a much more tentative association is made of the weak line at 3.455 eV with an exciton decaying at a neutral acceptor (I_1). Distant donor-acceptor pair spectra complete the near-gap emission.

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Piezoelectricity under Hydrostatic Pressure

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Phillips's theory of ionicity is used to estimate the piezoelectric coefficient under hydrostatic pressure of several semiconductors with a zinc-blende structure. It is found that this new effect is comparable in magnitude to the usual piezoelectric effect.

In 1960, Landauer[1] pointed out that the classical theory of pyroelectricity, which relates the existence or nonexistence of the pyroelectric effect to the symmetry of the crystal class, cannot be completely correct. Landauer points out that the presence of boundaries on the crystal breaks the symmetry of the crystal class so that symmetry considerations alone will not provide the complete answer. In this paper, we apply the same arguments to piezoelectricity. We will also given an estimate of the size of the piezoelectric effect arising from this symmetry breaking in several semiconductors based on Phillips's theory of ionicity.[2]

Consider GaAs. This has the zinc-blende structure. A crystal with surfaces perpendicular to the [111] direction can be viewed as consisting of alternate layers of Ga and As ions. Since the bonds are partially ionic in character, every unit of two layers will have a dipole moment. If one face of the sample consists of a Ga layer while the opposite face is an As layer, the sample will have a net dipole moment. However, compensating charges (electrons or other charges) will attach to the surface so as to cancel the static dipole moment.[3]

Consider a crystal in which only two parallel surfaces are perpendicular to the [111] direction. Since the crystal does not have inversion symmetry, the classical theory predicts that there is a piezoelectric effect under strain but that there is no effect under hydrostatic pressure. However, under hydrostatic pressure the size d of the unit cell is changed. Since the bonds are not purely ionic and since the homopolar and heteropolar parts of the band gap depend on d in different ways,[2] it is reasonable to expect the ionicity and therefore the dipole moment to change with d. If the compensating charges within the crystal cannot adjust quickly enough to the changing charge distribution, a piezoelectric effect can be observed even under hydrostatic pressure.

To estimate the size of the piezoelectric coefficent, we neglect any charge relaxation taking place at the surface. For instance, the charge on a Ga is assumed to be the same whether it is on the surface or inside. We expect this model to provide us with a reasonable estimate of the order of magnitude of the effect.

To calculate the charge density, we follow Phillips[2] and assume that only one Fourier component of the pseudopotential V is dominant. If $\vec{G}$ is the wave vector of the dominant component, we find, using Poisson's equation, that the ionic part of the charge distribution $\rho_i(\vec{G})$ is $(G^2/4\pi)V_1(\vec{G})$, where $V_1(\vec{G})$ is the antisymmetric part of the potential. The ionic charge distribution in coordinate space $\rho_1(x)$ is given by $(G^2/4\pi)V_i \sin Gx$. In GaAs, the (1, 1, 1) component of V is dominant. The piezoelectric coefficient is given by the change in the polarization per unit strain. If we assume that the two parallel surfaces are perpendicular to the [111] direction, the polarization P is given by one-half the surface charge density. The surface charge density is obtained by integrating $\rho_i(x)$ over a half-period, i.e., from 0 to π/G. We find $P=(G/4\pi)V_i(\vec{G})$.

Note that in the calculation of P, we need consider only that component of V_i which is perpendicular to the surface, since only that component contributes to the total dipole moment of the sample. The present calculation differs essentially from the usual calculation of the piezoelectric effect in which boundaries are not considered in detail. In that case, the sample is considered to have the symmetry of the crystal class so that all four equivalent (1, 1, 1) components of V_i must be taken into account. In the present calculation, the four (1, 1, 1) components are no longer equivalent. The boundary picks out the component which must be considered and there is no longer cancellation of the total dipole moment after addition of the contributions from the different components.

The piezoelectric coefficient e_{pol} is given by $d(\partial P/\partial d)$, where d is the size of the unit cell. Using the expression for P, we obtain

$$e_{\text{pol}}=\left[\frac{d}{V_i(\vec{G})}\left(\frac{\partial V_i(\vec{G})}{\partial d}\right)-1\right]P. \tag{1}$$

The change in the potential can be found by relating V_i to the heteropolar gap C. From Phillips,[2] we have $\frac{1}{2}C=2V_s(1,1,1)\,V_i(1,1,1)/\Delta T$, where V_s is the symmetric part of V and ΔT is the difference in kinetic energy between the (110) and (001) states, Note that ΔT is proportional to d^{-2}. Furthermore,[2] $V_s \propto d^{-2.5}$ and C is proportional to $d^{-1}e^{-k_s d}$, where the proportionality constant depends on the crystal and k_s^{-1} is the Thomas-Fermi screening length. Using the above, we find

$$e_{\text{pol}}=-0.5(k_s d+3)P. \tag{2}$$

For GaAs, $k_s d$ is approximately 2. Using Eq. (2) and $V_i\,(1,1,1)=0.07$ Ry,[4] we find that the value of e_{pol} is about -0.08 C/m^2. For comparison, we note that the experimental value of $(2\sqrt{3})e_{14}$ is -0.182 C/m^2.[5] In Table I we list the values of e_{pol} and $(2/\sqrt{3})e_{14}$ for several compounds with zinc-blende structure, and show that the hydrostatic effects should be observable.

TABLE I. e_{pol} for various crystals with a zinc-blende structure. For comparison, the experimental value of the ordinary piezoelectric coefficient $(2/\sqrt{3})e_{14}$ for the same crystals are given. The experimental values are taken from Ref. 5. The values of the pseudopotential which goes into e_{pol} are from Ref. 4.

	e_{pol}	$(2/\sqrt{3})e_{14}$
GaAs	-0.08	-0.182
GaP	-0.125	-0.116
InSb	-0.06	-0.082
ZnS	-0.25	$+0.170$

The configuration we have considered is not so unlikely since it corresponds to the minimum number of broken bonds at the surface.[1] This is relevant to the surface energy, since the bonds are mainly covalent in character. Other ways of terminating the crystal would lead to other (smaller) values of the dipole moment and hence e_{pol}, but only very special ways of terminating the crystal would give a vanishing value of e_{pol}.

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High-Field Hall Factor of n-Ge at 200 °K

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The high-field Hall factor of n-type germanium at 200 °K has been theoretically calculated including the effect of carrier scattering into the $\langle 100\rangle$ minima and that of the magnetic field dependence of the carrier temperature and population in the different valleys. The results calculated with the optical-phonon deformation-potential constant $D_0 = 0.4\times10^9$ eV cm^{-1} differ widely from the experimental values. Good agreement between theory and experiment is obtained for values of D_0 lying within 1×10^9 and 1.5×10^9 eV cm^{-1}.

I. INTRODUCTION

In a recent paper Heinrich *et al.*[1] reported experimental results on the hot-electron galvanomagnetic coefficients of n-type germanium at 200 °K. They have also shown that the results can be explained if the scattering of the electrons from the normally occupied $\langle 111\rangle$ valleys to the $\langle 100\rangle$ valleys at high fields is taken into account. The intervalley transfer into the $\langle 100\rangle$ minima has been calculated on the basis of a model introduced by Omar.[2] In this model the electron temperature has been taken to be the same for all the valleys and has been obtained from experimental values of the average drift velocity and of the energy relaxation time. Further, Heinrich *et al.*[1] have neglected the effect of the magnetic field on the temperature and the carrier population in the different valleys. This effect, though negligible at low fields, is likely to be important at large values of the heating field.[3] Reasonable agreement between theory and experiment has been obtained by Heinrich *et al.*[1] for the ratio of the longitudinal and the transverse magnetoresistance. The agreement for the high-field Hall factor is, however, only qualitative.

It is of interest to determine if the agreement between theory and experiment is improved if the effect of the magnetic field on the carrier distribution function and that of the temperature inequality of the $\langle 111\rangle$ and the $\langle 100\rangle$ valleys are taken into account.

In this paper we have calculated the Hall factor on the basis of a model that has been found useful in explaining the negative differential conductivity of uniaxially strained n-type germanium at room temperature.[4] We have also included the carrier repopulation effect of the magnetic field. The model together with the method of analysis has been presented in Sec. II. The numerical results are compared with the experimental data in Sec. III.

II. MODEL AND THE ANALYTICAL DETAILS

We have assumed that the symmetrical part of the distribution function in each valley is Maxwellian with an electron temperature determined by the field and the prevalent scattering mechanisms. According to the revised estimate of Stratton[5] the carrier concentration required for establishing a Maxwellian distribution through predominant carrier-carrier scattering is 10^{15} cm^{-3} at 200 °K. The carrier concentration in the experimental sample (3×10^{14} cm^{-3}) is not much lower than this critical concentration. In the case of n-type ger-