Table 3. Characteristics of the polymorphic transition in Ge

	Static data	Present work
Transition pressure (kb)	120–125[a]	114–122
Specific volume	$0\cdot875\ V_0$[b]	$0\cdot870\ V_0$–$0\cdot880\ V_0$[e]
Temperature (°C)	20	160[c]
$\Delta V/V$	$20\cdot7\%$[b]	—
dP/dT (kb $°\mathrm{C}^{-1}$)	—	$-3\cdot1\times10^{-2}$
ΔH (cal g^{-1})	—	$12\cdot5$[d]

(a) Ref. 10.
(b) Ref. 16.
(c) As estimated by McQueen, Ref. 13.
(d) Calculated using ΔV given by Jamieson, Ref. 16.
(e) Corrected to 20°C for comparison with static data.

one-dimensional elastic compressions which are uniquely achieved in the shock wave loading experiments. Resistivity measurements for large uniaxial elastic strains are of interest since they may be useful for confirming the theoretical calculations of KLEINMAN(2) and GOROFF and KLEINMAN(3) which predict the effect of a general strain tensor on the energy bands of silicon, and by inference, germanium. These measurements may also help to describe the so-called "anisotropic stress effect" observed for stressed semiconductor *p–n* junctions.(23)

The component of the energy gap change induced by volumetric compression has been verified by hydrostatic experiments, but the component of energy gap change induced by shear strain has not been verified since large shear strain components cannot be applied statically to brittle materials such as germanium. If the germanium samples behave intrinsically for large shear strain, it is possible that the resistivity measurements under shock compression can provide a measure of the energy gap change induced by shear strain. The conditions imposed on the sample by plane-wave shock loading in the elastic range are well defined allowing all stress and strain components to be accurately evaluated. Further, since the compressions are small the process is adiabatic to a very close approximation and accurate calculations can be made of the slight temperature rise (5·6°K at 44 kb)* induced by shock wave.

Previous attempts to measure energy gap changes induced by shear strain have included the measurement of reflectance from Ge samples subjected to bending stress.(25) Also, piezo-resistance measurements in uniaxial *stress* on heavily doped germanium specimens give deformation potential determinations on the motion of individual valley minima and the valence band maximum.(26) WORTMAN *et al.*(27) have used GOROFF and KLEINMAN's(3) theoretical predictions for silicon to predict the effect of various stress tensors on the band structure of germanium and thus the effect upon the characteristics of Ge *p–n* junctions. IMAI and UCHIDA(28) find this analysis to be consistent with their measurements of the characteristics of heavily doped Ge *p–n* junctions under uniaxial *stress*. Similarly, RINDNER(23) has applied uniaxial *stress* to Ge *p–n* junctions and found agreement in sign and qualitative behavior to that predicted by Wortman *et al.*

The effect of *pressure* on the resistivity of Ge has been extensively investigated and recently summarized in the excellent review by PAUL and WARSCHAUER.(29) The energy gap, E_g, is found to increase linearly with *pressure* to 15 kb at a rate of 5×10^{-3} eV kb^{-1}. From 15 kb to 30 kb the rate of increase of E_g decreases significantly. This has been shown to be consistent with the hypothesis that the minimum energy of the conduction band is shifted in k space. Further, effective mass changes of electrons with *pressure* are found to be only $\frac{1}{2}\%$ per kb, and the mobility of electrons is found to decrease only 0·4% per kb in the absence of intervalley scattering. Considerable correlation is found between the *pressure* dependence of any

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* The temperature of the shocked Ge in the elastic range is computed as $T = T_0(V_0/V)^\gamma$. Gruneisen's ratio, γ, was taken as 0·725 in agreement with the data of Ref. 24.

particular gap among all the diamond semiconductors; hence, the analysis of Goroff and Kleinman might be expected to predict the behavior of Ge under *pressure*. This is not to imply that the behavior under shear strain is analogous between Ge and Si, since there is insufficient theoretical or experimental evidence to make this judgment.

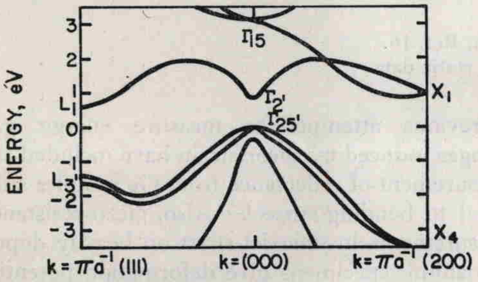

FIG. 4. Band structure of germanium. After Paul and Warschauer, Ref. 28.

The energy band structure for germanium is shown schematically in Fig. 4. The analysis of Goroff and Kleinman for silicon predicts that the conduction band minimum $L_1(111)$ is lowered with [111] one-dimensional strain,* that the degenerate $\Gamma'_{25(j=3/2)}$ valence band maximum is raised with [111] strain and that these positions retain their critical position in the band structure. The predictions are that the change, δ, in energy levels is:

$$\delta L_1(111) = 6{\cdot}20\Delta - 11{\cdot}5\epsilon, \tag{5}$$

and

$$\delta\Gamma'_{25(j=3/2)} = 2{\cdot}09\Delta + 2{\cdot}79\epsilon, \tag{6}$$

where Δ is the dilatation and ϵ is the [111] direction strain. The first terms show the effect of the dilatation, and the second terms are due to the dilatationless shear strain. Thus the change in energy gap, δE_g, is predicted to be:

$$\delta E_g = +4{\cdot}11\Delta - 14{\cdot}29\epsilon. \tag{7}$$

The shear strain contribution is clearly dominant for [111] one-dimensional strain. The dilatation part of the expression has been previously measured by PAUL and BROOKS,(30) hence, we look to our measurements for an evaluation of the shear strain contribution.

The results of the resistivity measurements in the elastic range are shown in Fig. 5 where the logarithm of the observed resistivity at wave transit time is plotted against strain. The logarithm of resistivity shows a linear decrease with strain indicating that the decrease of resistivity is due to an exponential term.

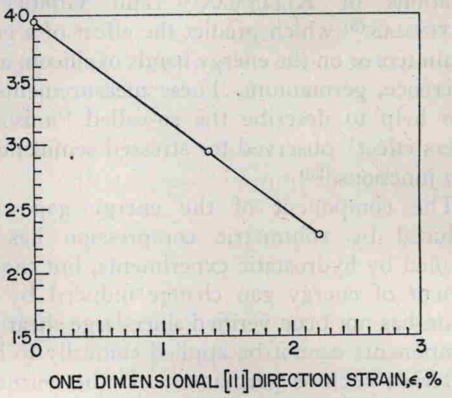

FIG. 5. Resistivity of [111] Ge in one-dimensional strain.

Since the intrinsic resistivity of a semiconductor is related to the energy gap by an exponential term, $\exp[E_g/2kT]$ and the terms involving the mobilities and effective masses of the carriers are pre-exponential factors, the exponential decrease of resistivity with strain indicates that the change is principally due to the strain-induced energy gap change. Assuming that the strained Ge exhibits intrinsic behavior and that the pre-exponential factors affecting the resistivity are unchanged from their atmospheric pressure values, an energy gap change can be calculated consistent with the measured resistivity. The value obtained is

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* A one-dimensional strain along the [111] axis as achieved in the shock wave experiment gives a strain tensor referred to the crystal axes of:

$$\frac{\epsilon}{3}\begin{bmatrix}1 & 1 & 1\\ 1 & 1 & 1\\ 1 & 1 & 1\end{bmatrix} = \frac{\epsilon}{3}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} + \frac{\epsilon}{3}\begin{bmatrix}0 & 1 & 1\\ 1 & 0 & 1\\ 1 & 1 & 0\end{bmatrix}$$

$$= \Delta + \frac{\epsilon}{3}\begin{bmatrix}0 & 1 & 1\\ 1 & 0 & 1\\ 1 & 1 & 0\end{bmatrix}$$

where ϵ is the strain along the [111] axis. This strain tensor is a combination of a dilatation, Δ, and a dilatationless shear strain.