TABLE I. Conversion fractions.

	c_{35}/c_{K35}	$c_{\gamma 35}$	c_{K35}
Electric dipole	1.13[a]	0.23	0.68
Magnetic dipole	1.10[a]	0.12	0.80
Electric quadrupole	3.16[a]	0.018	0.31
Present work	(1.1)[b]	0.078	0.84
Present work	(3)[b]	0.048	0.32

[a] For these calculations conversion in shells higher than the L shell has been neglected.

[b] Assumed values.

electric dipole, but would appear to be a mixture of magnetic dipole and electric quadrupole. This is in agreement with the shell structure model of M. G. Mayer,[9] which predicts a spin change of one unit without parity change.

We wish to thank Miss E. Wilson for valuable assistance.

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On the Mechanism of Impurity Band Conduction in Semiconductors

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In recent letters Hung and Gliessman[1] and Hung[2] have reported on the anomalous low temperature behavior of the resistivity and the Hall coefficient of germanium. Similar anomalies have previously been observed in silicon carbide by Busch and Labhart.[3] In connection with our work[4] on silicon carbide we have attempted to interpret the results of the last authors on the basis of a conduction mechanism in an impurity band formed by the interaction of the *excited* impurity states at high concentrations. We believe that our model, which differs somewhat from that given by Hung,[2] may be used also for germanium and can explain the deviations from the experimental curves of Hung's calculated values.

In a semiconductor with non-interacting impurity centers the Schrödinger wave equation

$$\nabla^2\psi+(2m^*/\hbar^2)(E-V)\psi=0, \tag{1}$$

where

$$V(r)=-e^2/\kappa r \tag{2}$$

has an infinite series of stationary solutions[5] corresponding to the discrete bound states

$$E_n=-2\pi^2m^*e^4/n^2\kappa^2h^2 \quad (n=1, 2, 3, \cdots) \tag{3}$$

of the electron or hole. $V(r)$ is the Coulomb potential between the bound electron or hole (at a radial distance r) and the corresponding ion, κ is an effective dielectric constant, m^* is the effective mass in the conduction or the filled band. An activation energy

$$E_{a0}=E_{n=1}=-2\pi^2m^*e^4/\kappa^2h^2 \tag{4}$$

is required for conduction and since the excited states are localized, their presence has no effect on the conduction mechanism. The right-hand portion of Fig. 1 shows the discrete levels of a donor-type impurity atom in a n-type semiconductor.

A wave function ψ_n corresponds to each energy level E_n, whose radial extent increases with n. As the impurity concentration is increased, neighboring atoms approach each other and overlapping begins between ψ_n's of the excited states. These states broaden into quasi-continuous band-like series which partly overlap each other and the conduction band in a manner shown in the central portion of Fig. 1.

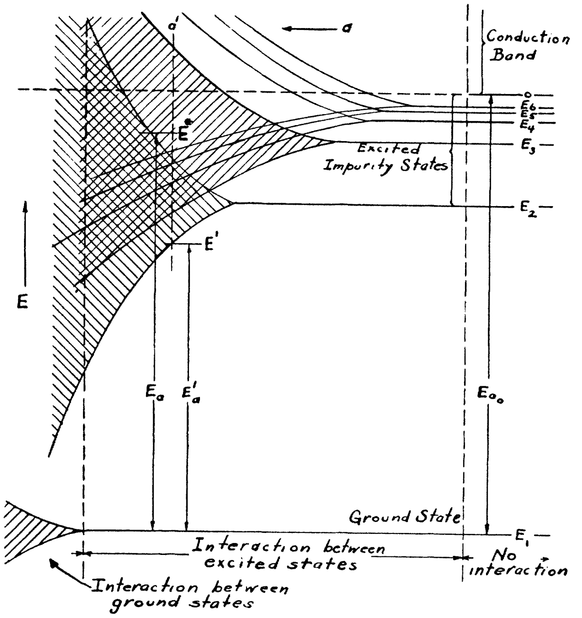

FIG. 1. Schematic representation of the broadening of the discrete impurity states with increasing concentration of donor-type impurity atoms in a n-type semiconductor. The average distance a between neighboring centers decreases in the direction of the arrow. E_a' is the low temperature activation energy giving low mobility electron conduction in the impurity band, E_a is the normal activation energy.

For a given concentration corresponding to an average distance a' between neighboring atoms, *a low temperature activation energy* E_a' may be defined, which is sufficient to take the bound electron from its ground state into a level E' where it can contribute to the conduction with a high but finite effective mass $m'>m^*$ and therefore a low mobility. At higher temperatures a greater number of electrons have higher energies and one can define the *normal activation energy* E_a as that required to take the bound electron into a level E^* (lower for higher impurity concentrations) where the density of the states is such that the effective mass of the electrons approximates to m^*.

The decrease of the normal activation energy E_a with increasing impurity concentration, first recognized theoretically by Shifrin,[6] has been observed in a large number of semiconductors including silicon[7] and germanium[8] but no satisfactory theory has been put forward so far. The existence of a lower activation energy E_a' affecting the low temperature behavior has not previously been considered. Hung and Gliessman's experimental curves of logρ *vs.* $1/T$ and log$R$ *vs.* $1/T$ at very low temperatures show small but definite slopes which indicate the presence of an activation energy. In Hung's interpretation of the impurity band conduction this energy is neglected and the calculated curves of the resistivity ρ and the Hall coefficient R are both flat. The approximate agreement obtained by Hung is based on the assumption that the carriers in the impurity band in an n-type crystal are electrons and those in a p-type crystal are holes. In our model this is explained by the fact that the impurity band formed by the excited states in an n-type crystal is empty at 0°K and partially filled at higher temperatures, so that conduction is of the electron type. The objections to a model which attributes conducting properties to a donor band in such a crystal are that: (a) the broadening of the ground states into a donor band requires very strong interaction between neighboring centers, i.e. very high concentrations, and (b) since such a donor band is completely filled at 0°K, any conduction at higher temperatures must be of the hole type.

A further point which our model may clear up in the case of germanium is the source of the extra scattering ions which Hung and Johnson[9] introduce in order to explain the resistivity curves at temperatures above that at which the anomaly begins. They attribute this resistivity to the Rutherford scattering by impurity ions[10] of concentration $N_s = n + N_0$, where n is the concentration of the conduction carriers and N_0 is provided by the loss of electrons from donor levels to lower lying acceptor levels. This model requires that the concentrations of donors and acceptors in a high resistivity sample should be nearly equal. This condition is not necessarily satisfied in practice. Such an assumption is not needed, however, if it is considered that in germanium, due to a small activation energy E_a', a large number of carriers are found in the conducting impurity band described above, so that an equal number of ions are provided which can act as scattering centers. The resistivity curves may therefore be explained satisfactorily on the basis of a single type of impurity.

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X-Ray Study of the Phase Transition in Lead Titanate

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IN a preceding note,[1] we have reported that the solid solution of $BaTiO_3$ and $PbTiO_3$ has the same type of crystal structure as that of $BaTiO_3$, and its tetragonality increases with lead contents, accompanying the rise of Curie temperature. Lead titanate has a larger tetragonality and a higher Curie temperature (*ca.* 490°C) compared with those of $BaTiO_3$. It may be expected that this crystal also transforms to cubic structure at the Curie point as in the case[2] of $BaTiO_3$. To examine this behavior precisely, we have performed an x-ray study on the temperature change of lattice parameters.

We used the ceramic specimens prepared by sintering the mixture of PbO and TiO_2 at about 1100°C. These ceramics were pulverized to fine powder and sealed in a very thin capillary tube made of hard glass (diameter = 0.5 mm). The Debye photographs were taken at temperatures from 30 to 535°C, using CuK_α-radiation. The camera length is 55.5 mm. The precise lattice constants and the axial ratio were calculated mainly from (143) and (134) lines on photographs taken by the back reflection method. These results are shown in Figs. 1 and 2.

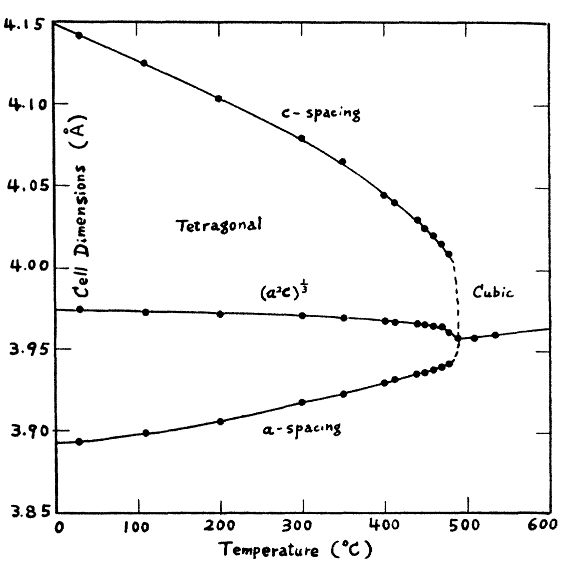

FIG. 1. Lattice parameters as a function of temperature.

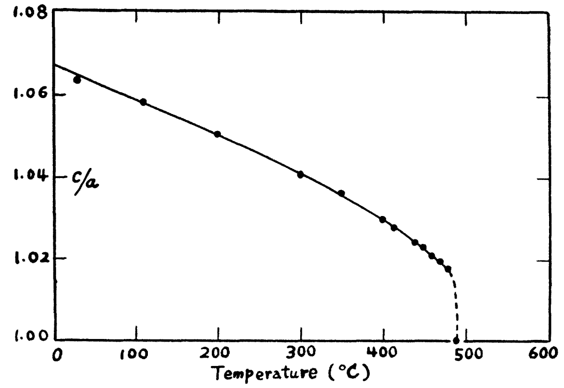

FIG. 2. Axial ratio as a function of temperature.

The photograph at 30°C clearly shows the tetragonal structure with $a = 3.894A$, $c = 4.140A$, and $c/a = 1.063$. These results are in agreement with those of other authors.[3] When the temperature is raised, this axial ratio decreases gradually until the structure changes to a cubic lattice at about 490°C, in accordance with our permittivity measurement. At 535°C, the lattice constant $a = 3.960A$.

It is remarkable that, as is shown in Fig. 3, the volume of unit cell does not increase but decreases slightly with the temperature rise, and during the transitional region it diminishes nearly discontinuously by the amount $\Delta v/v = 4.4 \times 10^{-3}$; i.e., $0.27A^3$ per unit cell. It seems reasonable to suppose that the thermal expansion of $BaTiO_3$-type ferroelectrics is a superposition of the normal expansion and abnormal contraction which is caused by the temperature change of polarization. It seems that in this crystal the latter effect is large enough to cover the former. The volume expansion coefficient of this crystal is given approximately by $\alpha = -1.6 \times 10^{-5}$/deg. in the tetragonal region, and $\alpha = 2.5 \times 10^{-5}$/deg. in the cubic region. A preliminary dilatometric measurement is in good agreement with the x-ray data.

After all, it will probably be said that the phase transition in $PbTiO_3$ is of the barium titanate type, but is more drastic in several points. In addition, we have measured the permittivity at temperatures from −170 to 550°C, and found only one transition, in contrast with $BaTiO_3$, which shows three transitions in this temperature range. We are now studying the anomalous specific heat at this transition. Detailed results will be reported shortly in the *Journal of the Physical Society of Japan.*

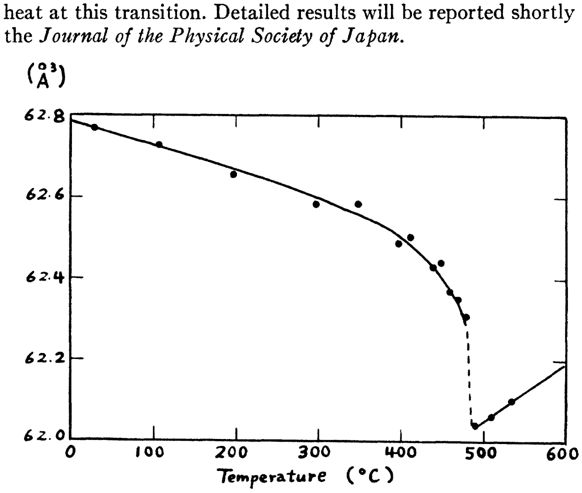

FIG. 3. Unit cell volume as a function of temperature.