its negative under time inversion. Consider then, for example, the matrix element

$$\begin{aligned}\langle\Psi_1{}^\alpha|L_z+2S_z|\Psi_1{}^\alpha\rangle &= \langle K\Psi_1{}^\alpha|K(L_z+2S_z)K^{-1}|K\Psi_1{}^\alpha\rangle^* \\ &= -(-1)^{\frac{3}{2}+\frac{3}{2}}(-1)^{\frac{3}{2}+\frac{3}{2}}\langle\Psi_4{}^\alpha|L_z+2S_z|\Psi_4{}^\alpha\rangle \\ &= -\langle\Psi_4{}^\alpha|L_z+2S_z|\Psi_4{}^\alpha\rangle. \qquad \text{(B5)}\end{aligned}$$

We see that the matrices $\mathbf{U}^1$ and $\mathbf{U}^2$ in Table II have this property so that time reversal does not influence the fact that we have two constants g_1 and g_2. (If, on the other hand, L_z+2S_z were a Hermitian operator, even under time inversion all matrix elements of all components of this operator between these states would vanish, i.e., $g_1=g_2=0$.) In a similar way, we can see that time reversal does not influence the number of constants in the two-by-four block or in the two-by-two block. It does, however, cause g_4 to be real. (g_1, g_2, and g_3 are obviously real since we are dealing with a Hermitian operator.)

In general, time reversal can influence the number of independent constants necessary to determine matrix elements of symmetric operators. Arguments of the type given in Eq. (B5) will determine how the number of constants is influenced.

APPENDIX C

The basis for the sublevels of spin 5/2 was chosen to be that given by Rose.[7] The unitary matrix which transforms this basis to two sets of functions transforming like $\Gamma_8{}^+$ and $\Gamma_7{}^+$ can be found by the method given in reference 9. Performing the corresponding similarity transformation of the Hamiltonian matrix (12) allows one to identify terms in the transformed matrix (12) with those of (19) and thus to get the relations between the constants.

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Conductivity of Grain Boundaries in Grown Germanium Bicrystals

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The conduction of current in the grain boundary of a grown germanium bicrystal has been studied as a function of doping. For all samples, the behavior shows only a small temperature dependence from 2–300°K. The conduction in the grain boundary is ohmic if no secondary effects are introduced by conduction in the bulk material. Samples with no doping and with *n*-type, *p*-type, or copper doping are all characterized by having a resistivity of about 3000 to 11 000 ohms per square. The lack of a strong dependence on doping indicates that the grain boundary behavior is not due to the segregation of impurities at the boundary.

THE nonohmic character for current flow perpendicular to grain boundaries in *n*-type germanium was found in early work on polycrystalline material.[1,2] This means that the grain boundary is a *p*-type layer, forming an *n–p–n* structure. In *p*-type germanium, this nonohmic behavior disappears but photoelectric measurements show that the grain boundary now acts as a p^+-type layer.[3] The *p*-type nature of the grain boundary was confirmed by Tweet[4] using measurements of the Hall effect for current flow in the grain boundary sheet of gold-doped germanium bicrystals. A partial explanation of this behavior was given by Taylor, Odell, and Fan[5] in terms of the formation of a double Schottky barrier about the grain boundary due to charges in surface states which may arise either from lattice misfit or segregation of acceptor type impurities at the boundary. The misfit at the grain boundary, according to the model proposed by Read[6] for dislocations and extended to grain boundaries by Mataré[7] causes "dangling bonds." These dangling bonds are able to pick up electrons in a lower energy state until the energy lost by adding an electron is compensated by the energy increase due to electron repulsion. On the other hand, the possibility that the behavior may be due to impurities is present in Tweet's experiment where gold is an acceptor that may not completely deionize at the lowest temperatures used. In other cases the *p*-type layer has been attributed to the segregation at the boundary of copper which is an acceptor.

In a study of the effect of impurities on grain boundary behavior, measurements of the current in the grain boundary were made for a variety of crystal dopings. The work was performed on carefully oriented bicrystals[8] grown by the vertical pulling technique with [100] seeds symmetrically tilted about the [010] axis at

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[1] K. Lark-Horovitz, National Defense Research Committee Report NDRC-14-585, 1945 (unpublished).

[2] G. L. Pearson, Phys. Rev. **76**, 459 (1949).

[3] Weinreich, Mataré, and Reed, Electrochemical Society Meeting, Washington, D. C., May 12–16, 1957 (enlarged abstracts).

[4] A. G. Tweet, Phys. Rev. **99**, 1182 (1955).

[5] Taylor, Odell, and Fan, Phys. Rev. **88**, 867 (1952).

[6] W. T. Read, Jr., Phil. Mag. **45**, 775 (1954).

[7] H. F. Mataré, Z. Naturforsch. **10a**, 640 (1955).

[8] H. F. Mataré and H. A. R. Wegener, Z. Physik **148**, 631 (1957).

angles of 10–30°, most frequently at 20°. The intrinsic starting material was either undoped, doped with *p*-type (Ga) or *n*-type (Sb) impurity, or diffused at 760°C with about 10^{16} copper atoms/cm^3. Samples approximately $1\times1\times10$ mm were cut with the axis parallel to the [010] tilt axis. In order to study the flow of current in the grain boundary region, it is necessary to minimize the parallel flow in the bulk material. This may be accomplished by using contacts which are ohmic on the grain boundary and rectifying on the bulk. For *n*-type material, alloyed indium contacts enable measurements to be taken from 2–300°K. A second approach is possible if the grain boundary conduction persists at temperatures where bulk conduction is negligible because of the de-ionization of donors and acceptors. For Group III or V impurities it is necessary to operate at liquid helium temperature and use only moderate doping to avoid impurity band conduction. These measurements were made by placing the samples in the chamber of a Collins helium liquefier and allowing the chamber to warm up slowly to obtain temperature variation. The temperature readings were taken on the liquefier thermometer and also from a carbon resistor. The resistor was compared with the liquefier thermometer with check points at liquid helium and nitrogen temperatures in order to smooth the temperature curve.

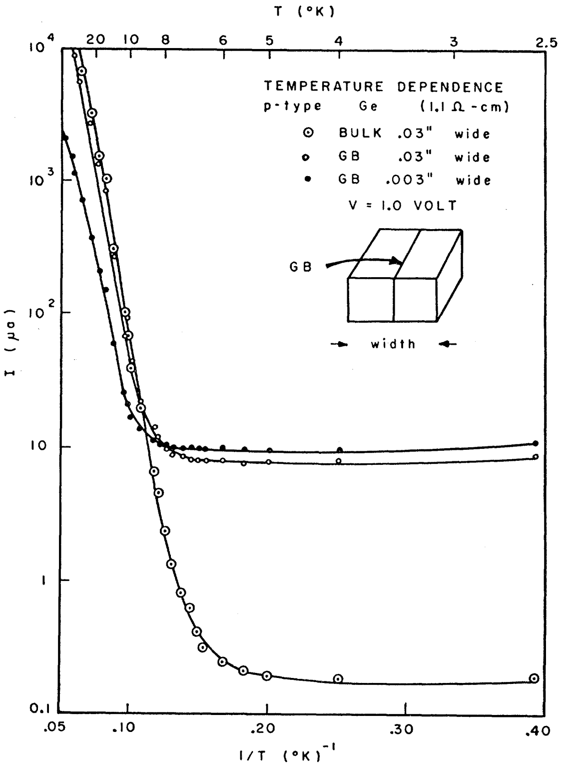

FIG. 1. Semilogarithmic plot of temperature dependence of current in grain boundary and bulk samples with ohmic contacts.

Conduction in the grain boundary sheet was investigated as a function of temperature and voltage. In Fig. 1 the temperature dependence for 1.1 ohm-cm *p*-type bulk and grain boundary samples with ohmic contacts are shown. Below 5°K there is a ratio of conductivities of 50:1 between the grain boundary and bulk samples and there is also no dependence on the dimension perpendicular to the grain boundary, which

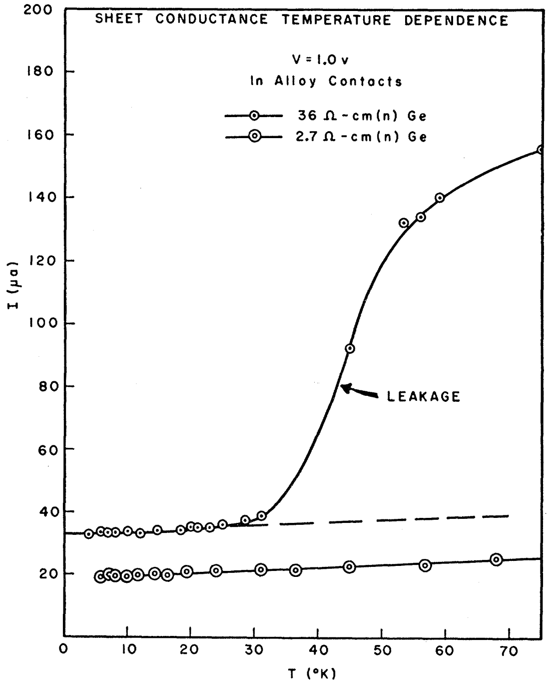

FIG. 2. Temperature dependence of grain boundary current in samples with rectifying contacts to minimize bulk conduction.

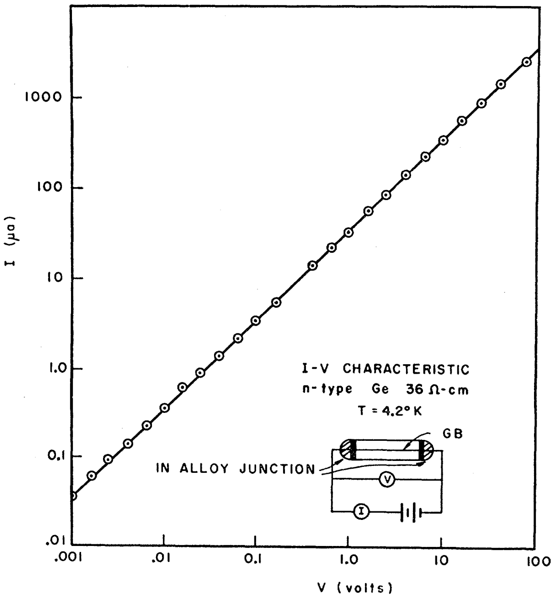

FIG. 3. Log-log plot of $I-V$ characteristic of grain boundary conduction in samples with rectifying contacts at 4.2°K.

TABLE I. Dependence of grain boundary sheet resistivity ρ^* on doping of crystal.

Sample No.	ρ (bulk) $T=300°K$ (ohm-cm)	Type	Impurity N (atoms/cc)	Type	ρ^* (ohms per square) $T=4.2°K$
7	1.3	n	1.4×10^{15}	Sb	7800
42	1.6	n	1.1×10^{15}	Sb	5100
6	2.7	n	7×10^{14}	Sb	7500
17	4	n	4.5×10^{14}	Sb	3600
3	5	n	4×10^{14}	Sb	3600
35	27		intrinsic		3600
64	30		intrinsic		5600
29	36		intrinsic		4100
31	4	p	2×10^{14}	Ga	11200
9	1.75	p	3×10^{14}	Ga	8200
11	1.1	p	8×10^{14}	Ga	10200
12	1.1	p	8×10^{14}	Ga	11200
27			10^{16}	Cu	2900
15			10^{16}	Cu	3700
(Tweet[a])				Au	8000

[a] See reference 4.

indicates that the predominant current flow is in the grain boundary. The flattening of the current at low temperatures for the bulk sample is probably due to impurity band conduction. The range of independence from temperature change of grain boundary conduction shown in Fig. 1 is extended to higher temperature in Fig. 2 where rectifying contacts to the n-type germanium prevent parallel conduction in the bulk material. In the 2.7 ohm-cm sample the behavior is essentially independent of temperature up to 300°K although it is only shown to 70°K. The 36 ohm-cm sample shows a temperature-independent behavior to 30°K where the poor characteristic of the junctions allows a parallel leakage path for current through the bulk material. The same temperature independence was found by Tweet in gold-doped bicrystals of the same orientation. The temperature measurements were made in the ohmic range.

The voltage dependence of grain boundary conduction is ohmic in all cases, at least for small applied voltages. In Fig. 3 an I-V characteristic is shown which is linear over greater than six decades up to a field of 50 volts/cm. This sample is high-resistivity material with rectifying contacts. In doped samples with ohmic contacts, the bulk material begins to conduct strongly at fields of 5–10 volts/cm due to impact ionization of the impurities. If rectifying contacts are used so that the voltage across the bulk is dropped primarily at the reverse-biased junction, then the voltage difference between the bulk and grain boundary conduction layer introduces a saturating behavior in the I-V characteristic at higher voltages. Using values in the linear range, the isolated grain boundary conduction can be characterized by a sheet resistivity ρ^* per square without reference to the thickness of the conducting sheet. In Table I, the behavior of variously doped samples is shown. The values of ρ^* range from 3000–11 000 ohms per square for these samples. This table supports the idea that the grain boundary conductivity is not due to the segregation of impurities—including copper—at the boundary.

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Temperature Dependence of the Breakdown Field of Barium Titanate

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The dc breakdown field has been measured for ceramic $BaTiO_3$ as a function of the ambient temperatures. The breakdown field shows, in general, a temperature dependence of the thermal breakdown type where the breakdown field decreases as the temperature is increased. However, in addition to this general behavior, the breakdown field dips down strongly and shows minima at the critical temperatures of the phase transformations. This seems to indicate a process of polarization breakdown, and is most pronounced near the orthorhombic-tetragonal transition temperatures.

1. INTRODUCTION

THE breakdown field (E_b) of ceramic $BaTiO_3$ has been measured by Vul, Gol'dman, and Razbush[1]; and Sarafanov[2] with an applied dc field; and by Sarafanov and Skanavi[3] with an applied ac field. Vul *et al.* concluded that there is no correlation between E_b and the dielectric constant, while Sarafanov and Skanavi proposed an inverse dependence of E_b on the electrical conductivity. It is felt that the conclusions of these authors may be based on insufficient experimental data for the following reason: while all the above authors cover a wide temperature range (from about 20°C to 200°C), measurements were made at only five to ten different temperatures. Since $BaTiO_3$ undergoes a crystallographic phase transformation from the tetragonal phase to the cubic phase at 120°C, the tetragonal phase being ferroelectric and the cubic phase being paraelectric, one might expect that this transformation could influence E_b and because of this, the temperature dependence of E_b might be rather complicated in the temperature region where these authors made their

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[1] Vul, Gol'dman, and Razbush, Zhur. Eksptl. i Teoret. Fiz. **20**, 465 (1950).

[2] V. I. Sarafanov, Zhur. Eksptl. i Teoret. Fiz. **27**, 590 (1954).

[3] V. I. Sarafanov and V. I. Skanavi, Zhur. Eksptl. i Teoret. Fiz. **27**, 595 (1954).