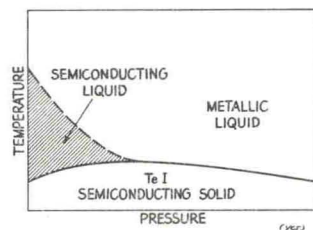FIG. 4. Qualitative phase diagram for tellurium showing the quasiphase boundary of the liquid state.

as the weighted sum of a metallic and a semiconductive component, the weight being a statistical Boltzmann factor governing the probability of the dissociation of the chain bonds. Therefore, the onset of metallic conduction can be interpreted as the temperature at which dissociation of the chain structures in the liquid has become prevalent and the liquid becomes progressively a disordered array of atoms with a metallic type conduction and bonding.

On the basis of the present study and resistance measurements on tellurium,[10] it is felt that the maximum in the melting curve of tellurium is intimately connected with the above behavior and structure of liquid tellurium. Measurements of the resistance of tellurium in the liquid state at pressures above the pressure of the melting-curve maximum show that conduction is metallic in nature at temperatures just above the melting point. On the basis of the above structure model for liquid tellurium, this indicates that pressure inhibits the preservation of the chain structure upon melting. The minimum in the volume versus temperature curve for liquid tellurium at atmospheric pressure indicates that the volume occupied by the atoms in the chain structure is greater than that occupied by an equal number of atoms in the structure of metallic-type conduction. Therefore, a lowering of the characteristic temperature associated with the change to metallic bonding is exactly what is expected. This lowering is entirely equivalent to the above-mentioned pressure inhibition of the temperature range in which the chain structure exists. As a consequence, it is felt that liquid tellurium undergoes a relatively ill-defined structure change which is inhibited by pressure. It now seems possible to establish the existence of a liquid state quasiphase[49] boundary, qualitatively shown by the dashed line in Fig. 4. The pressure inhibition of this quasitransition is responsible for a marked increase in coordination with pressure, possibly of such a nature as to yield densities of the liquid state greater than those of the corresponding solid. This semiconducting liquid to metallic liquid quasiphase transition is thus quite possibly a factor contributing to the melting curve maximum for tellurium.

An attempt to establish an effective boundary for the liquid semiconducting phase by resistance measure-

ments was made. Since this range of pressures and temperatures constitutes a region in which it is difficult to make measurements in our apparatus, we were unable to obtain reliable and consistent results. However, the metallic conduction of liquid tellurium at pressures above 10 kbar appears consistently.

Liquid-state studies of selenium at atmospheric pressure indicate that the chain structure is retained above the melting temperature and that liquid selenium remains a semiconductor with predominant electrical conduction by holes.[50,51] Blum et al.[51] also indicate the expectation that, at higher temperatures, liquid selenium will become metallic in nature. Because of the close similarity between the structure and properties of selenium and tellurium, it is believed that selenium will exhibit a melting-curve maximum analogous to that observed for tellurium. This maximum, if actually observed, could quite possibly be due to the dissociation of the chain structure in selenium at high pressures such as appears to be the case for tellurium.

A. von Hippel[18] has pointed to the progressive crystal structure development of the Group VI B elements. Recent x-ray investigations by McWhan and Jamieson[20] have shown that at pressures just above 40 kbar tellurium transforms to the β-polonium structure. It therefore seems possible that pressure will serve to bring all the Group VI B elements to the same crystal structure, i.e., the metallic polonium structure. On this basis, one is tempted to predict a melting-curve maximum for sulfur. However, the situation may be more complicated for sulfur than the above argument indicates, as pressure would first, perhaps, have to induce transformation to the chain-like hexagonal structure of Se and Te before transformation to the β-polonium structure could occur.

It is interesting to note that Bi, Sb, and Ge, which have melting curves with negative slopes, undergo a decrease in resistivity ρ upon melting followed by a metallic-type conduction in the liquid state,[52] just as tellurium does from 10 to 29 kbar. The possibility of correlation of the sign of the slope of the melting curve with the nature of the changes in resistivity upon melting is immediately apparent. Sutra,[53] and Schneider and Heymer[52] have found that an approximately linear relationship exists between the normalized change in resistivity $(\Delta\rho/\rho)$ and the relative volume change $(\Delta V/V)$ upon melting, for a number of elements. Since the Clapeyron equation relates ΔV to the slope of the melting curve and ΔS, the obvious extension of the above correlation is a comparison of $(\Delta\rho/\rho)$ and the initial

[49] The statistical nature of the liquid structure change as indicated by the work of Johnson (see Ref. 45) rules out the possibility of giving this change the status of a true phase boundary.

[50] H. W. Henkels and J. Maczuk, J. Appl. Phys. **25**, 1 (1954).
[51] A. I. Blum, N. P. Mokrovskii, and A. R. Regel, Izv. Akad. Nauk SSSR, Ser. Fiz. **16**, 139 (1952) [English abstract transl.: Chem. Abstr. **46**, 10753b (1952)].
[52] A. Schneider and G. Heymer, in *Proceedings of the National Physical Laboratory Symposium No. 9* (Her Majesty's Stationery Office, London, 1959), Vol. II, p. 1.
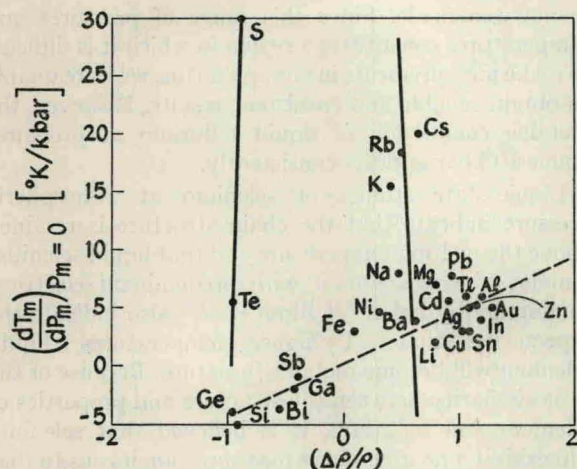[53] Genevieve Sutra, Compt. Rend. **234**, 2589 (1952).

FIG. 5. Correlation of the change in resistivity upon melting with the slope of the melting curve for a number of elements at atmospheric pressure.

slope of the melting curve $m_0 \equiv dT_m/dP_m$ at $P_m = 0$.[54] Figure 5 gives a plot of m_0 versus $(\Delta\rho/\rho)$.[55] A surprising regularity exists in the points lying in close proximity to the dashed line. The alkali metals and Group VI B elements comprise obvious exceptions to this correlation. The most general feature exhibited by Fig. 5 is the direct correspondence between the sign of $(\Delta\rho/\rho)$ and the sign of m_0. This correspondence is violated only by the Group VI B elements for which $(\Delta\rho/\rho) < 0$ and $m_0 > 0$.

To the authors' knowledge, the theoretical investigations concerning the change in resistivity upon melting have dealt only in an approximate manner with metals whose resistivity increases upon melting. Cusack and Enderby[56] have surveyed and evaluated these works which are based largely on Mott's[57] early attempts to relate the change in resistivity to ΔS.

[54] The elements and the corresponding sources for experimentally determined m_0 are: S, Se, Te: present work; Li, Na, K, Rb, Cs: R. C. Newton, A. Jayaraman, and G. C. Kennedy, J. Geophys. Res. 67, 2559 (1962); Ag, Mg: Ref. 21; Ge, Sn, Si: Ref. 28; Ba: Ref. 33; Fe, Ni: H. M. Strong and F. P. Bundy, Phys. Rev. 115, 278 (1959); Al, Ga, In, Tl: Ref. 27; Pb: M. L. McDaniel, S. E. Babb, Jr., and G. J. Scott, J. Chem. Phys. 37, 822 (1962); Bi: P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1952), p. 189. Values of m_0 for Au and Cu were calculated using Clapeyron's equation and atmospheric pressure values of ΔV and ΔS taken from O. Kubaschewski, Trans. Faraday Soc. 45, 931 (1949).

[55] All values of $(\Delta\rho/\rho)$ were taken from Ref. 52 except: S, Ref. 13, p. 58; Si and Ni, Ref. 56.

[56] N. Cusack and J. E. Enderby, Proc. Phys. Soc. (London), 75, 395 (1960).

[57] N. Mott, Proc. Roy. Soc. (London) A146, 465 (1934).

There is one further point of interest concerning the correlation of the initial melting-curve slopes with the general properties of the elements. In general, the melting of a substance is accompanied by marked changes in the long-range order of the crystal structure. However, most liquid metals exhibit a short-range order in close agreement with that of the corresponding solid.[52] While, conversely, the semimetals (e.g., Bi, Ge, and Ga, which have $m_0 < 0$) exhibit decided changes in both short-range and long-range order upon melting.[52] In fact, the x-ray diffraction patterns indicate a short-range order for the semimetals similar to those of the liquid metals.[52] Also, for most of the semimetals $\Delta V < 0$. This is not surprising since the short-range order of the semimetals is similar to that of the more closely packed liquid metals, and one would expect the relative volume of a substance to be more closely related to its short-range than its long-range order. Since $\Delta V < 0$ for these semimetals, $m_0 < 0$. Thus, for a number of elements, there appears to exist a direct relation between the sign of the slope of the melting curve m_0 and the change in short-range order upon melting. Presuming that such a relation is valid for all elements, and recalling that the short-range order for the Group VI B elements is preserved upon melting, we have then a better understanding of the failure of the Group VI B elements to conform to the direct correlation of the sign of $(\Delta\rho/\rho)$ and m_0. Also, it should be noted that the previously given explanation for the maximum in the melting curve of tellurium is in complete accord with this picture of the relation between the relative liquid and solid structures of the elements and the sign of the melting-curve slope. However, an explanation, on the basis of this model, of the maxima in the melting curves of elements with relatively close packed structures, such as barium, is not apparent.

All of the above observations and generalizations are by no means complete in themselves. A thorough survey and investigation of these properties of the elements is needed.

ACKNOWLEDGMENTS