

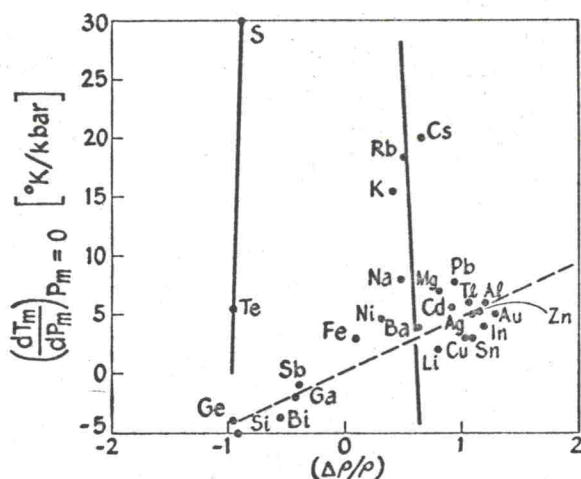


FIG. 5. Correlation of the change in resistivity upon melting with the slope of the melting curve for a number of elements at atmospheric pressure.

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 Enderby⁵⁶ have surveyed and evaluated these works which are based largely on Mott's⁵⁷ 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.

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