Figure 5. Electrical resistance of BiI_3 as a function of pressure at constant temperature.

transformation were taken as the transformation pressure for each cycle.

The existence of an $\alpha \rightleftarrows \beta$ transition in BiI_3 shown in Figure 4 was indicated in the phase diagram work on the Bi–BiI_3 system by Yosim, et al.,[8] although these authors could not unambiguously assign their thermal halts at 285 and 298° to definite phase transitions. No indication of a phase change in BiI_3 was found here which corresponds to the thermal halt at 285° in the Bi–BiI_3 system. However, it appears that the thermal arrest reported by Yosim, et al.,[8] at 298° corresponds to the $\alpha \rightleftarrows \beta$ transition in BiI_3 shown in Figure 4. This transition is not readily detected by thermal analysis but exhibits a discontinuity in the resistance vs. temperature curves. This is seen in Figure 6, which shows the electrical resistance of BiI_3 as a function of temperature at a constant pressure of 10.8 kbars. The $\alpha \rightleftarrows \beta$ transition occurs at 405° at this pressure. The $\beta \rightleftarrows$ liquid transition occurs over the temperature interval from 545 to 595°. The principal cause of this melting or freezing over such a wide interval is due to the pressure drop across the relatively long sample used in the resistance measurements. As stated above, this pressure drop may be of the order of 2–3 kbars. Since dT/dP for BiI_3 ($\beta \rightleftarrows l$) is 17.5°/kbar (Table I), such a pressure differential might be expected to give a melting range of 35–55°. The dta method gives a sharper indication of the melting and freezing points at elevated pressures than the above resistance method since in the former case the salt sample is contained in a relatively short ampoule which is in direct contact with the thermocouple junction. Nevertheless, as shown in Figure 4, relatively good agreement is obtained between the two methods.

This resistance discontinuity in BiI_3 at the $\alpha \rightleftarrows \beta$ transition was found by Fischer[20] at atmospheric pressure but was attributed by him to a "premelting" phenomenon. However, our measurements indicate that this is a solid–solid phase transition. Rosztoczy
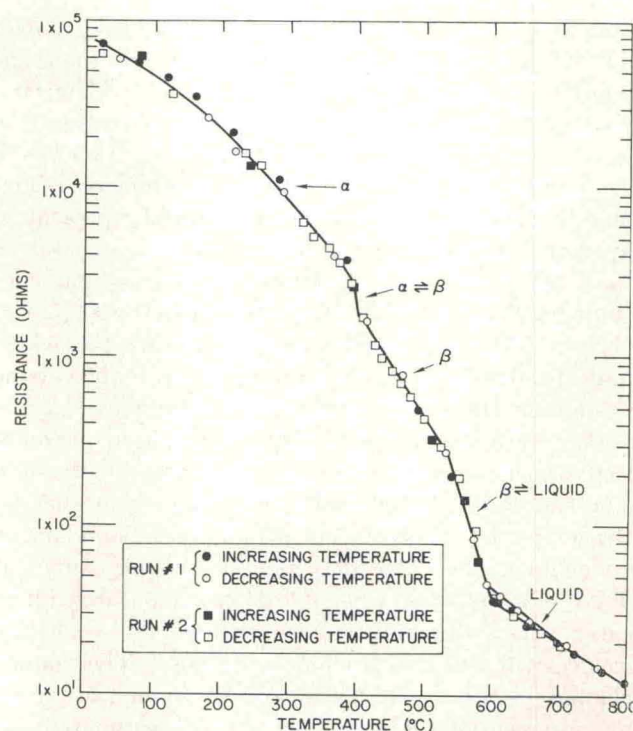

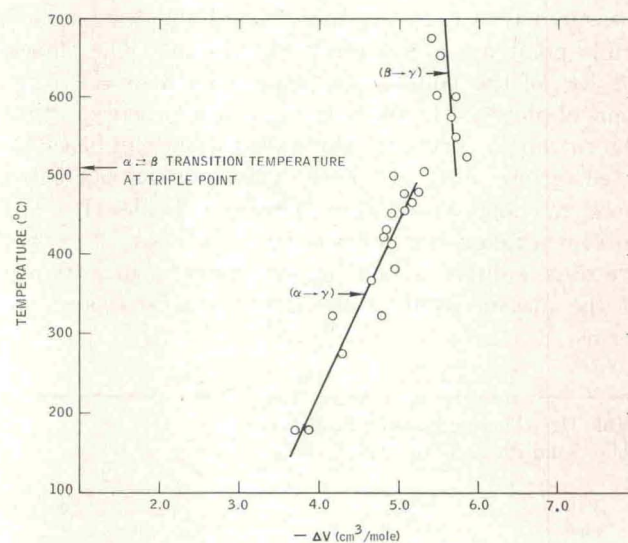Figure 6. Electrical resistance of BiI_3 as a function of temperature at a constant pressure of 10.8 kbars.

Figure 7. Transition volumes for the $(\alpha \rightarrow \gamma)$ and $(\beta \rightarrow \gamma)$ phase changes in BiI_3.

and Cubicciotti[21] and Cubicciotti and Eding[22] failed to find this $\alpha \rightleftarrows \beta$ transition in BiI_3 by thermal analysis[21] and by drop calorimetry.[22] The $\beta \rightleftarrows \gamma$ transition, like the $\alpha \rightleftarrows \gamma$ transition, was detected by both the volume discontinuity (Figure 5) and ac resistance techniques. The triple point for solid phases $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ occurs at

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(21) F. E. Rosztoczy and D. Cubicciotti, J. Phys. Chem., 69, 124 (1965).

(22) D. Cubicciotti and H. Eding, ibid., 69, 3621 (1965).

25.5 kbars and at 510°. The phase boundary slopes, dT/dP, for the phases in equilibrium around the triple point are: $\alpha \rightleftarrows \beta$, 5.5°/kbar; $\alpha \rightleftarrows \gamma$, $-375°$/kbar; and $\beta \rightleftarrows \gamma$, $-1000°$/kbar. The transition volumes for the $\alpha \rightleftarrows \gamma$ or $\beta \rightleftarrows \gamma$ transitions were measured from 175 to 675° by the volume discontinuity method of Bridgman.[13] The data points shown in Figure 7 represent an average of the transition volumes (ΔV_{tr}) obtained from the compression and decomposition processes at constant temperature. The discontinuity in the ΔV_{tr} vs. T curve at 510° is in agreement with resistance data which indicate a triple point at this temperature. The volume change for the $\alpha \rightleftarrows \beta$ transition was measured at one temperature only, 450°. These transition volumes were measured isothermally while varying the pressure. The results illustrated in Figure 4 show that the isotherm at 450° intersects this $\alpha \rightleftarrows \beta$ phase boundary at an acute angle. The detection or the measurement of ΔV of a transition when dT/dP is small is difficult to carry out isothermally. Nevertheless, the transition was carried out in this manner at 450°. The volume change for the $\alpha \rightarrow \beta$ transition determined by direct measurement is 0.1 cm³/mole with an estimated uncertainty of $\pm$ 0.1 cm³/mole. This is in fair agreement with $\Delta V(\alpha \rightarrow \beta)$ from $\Delta V(\beta \rightarrow \gamma) - \Delta V(\gamma \rightarrow \alpha)$ of 0.4 ± 0.4 cm³/mole. Thus the three independently measured transition volumes around the $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ triple point are approximately additive. The slopes, dT/dP, of the boundaries between each of the three pairs of phases in equilibrium were also measured; thus the entropies, ΔS, of the three transitions can be calculated by use of eq 1. These values of ΔS calculated from ΔV and dT/dP are shown in Table II. The entropy changes around the triple point $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ are thus additive within the experimental uncertainty of the measurement of the separate dT/dP and ΔV terms.

Table II: Thermodynamic Properties of Solid–Solid Phase Transitions in BiI_3

Phase change	dT/dP, deg/kbar	ΔV, cm³/mole	ΔS, eu
$\alpha \rightarrow \gamma$	-375	-5.3 ± 0.2	0.33
$\beta \rightarrow \gamma$	-1000	-5.7 ± 0.2	0.13
$\alpha \rightarrow \beta$	5.5	0.1 ± 0.1	0.43

Discussion

If data are available for ΔV and ΔS of fusion, then an independent check of the pressure dependence of the melting temperature dT/dP can be made by means of eq 1. Neither volumetric nor entropy data are available for the fusion of BiF_3. Data for the entropy of fusion are available for $BiCl_3$,[23] $BiBr_3$,[24,25] and BiI_3.[26] However, no direct determination of the volume of fusion of the bismuth trihalides has been

reported. An indirect determination of ΔV_f is sometimes made from density of the liquid and of the solid phases at the melting point. Densities for the liquid salts $BiCl_3$, $BiBr_3$, and BiI_3 near their melting points have been determined by Cubicciotti and co-workers.[27-29] Data necessary to calculate the densities of the solid phases of $BiCl_3$, $BiBr_3$, and BiI_3 at their melting points are not available. Lattice parameters at 25° are available;[6] however, $BiBr_3$ and BiI_3 undergo phase transitions between room temperature and their melting points. Furthermore, the necessary thermal expansion data between 25° and the melting points are not available. It is noted that the densities of solid $BiCl_3$ and $BiBr_3$ calculated from the room temperature lattice parameter and space group assignments of Wolten and Mayer[6a] are less than the densities of the corresponding liquid salts at their melting points.[27,28] The densities of solid $BiCl_3$ and $BiBr_3$ calculated from Wolten and Mayer's data are 3.86 and 3.80 g/cm³, while the densities of the liquid salts at their melting points measured by Keneshea and Cubicciotti[27,28] are 3.94 and 4.72 g/cm³. From the slopes of the fusion curves, Figures 2 and 3, however, we see that the solids must be denser than the liquids.

On the other hand, if the experimentally determined[30] densities of 4.75 and 5.7 g/cm³ for $BiCl_3$ and $BiBr_3$, respectively, and 5.78 g/cm³ for $BiI_3(\alpha)$[6b] are compared with Cubicciotti's densities for these molten salts, then it is seen that an over-all volume increase of about 20% occurs in going from the solid at room temperature to the liquid state at its normal melting temperature.

The initial pressure dependence of the melting temperature $(dT/dP)_{P=0}$ and the entropy of fusion data available from the literature have been used to calculate the volume of fusion ΔV_f of $BiCl_3$, $BiBr_3(\beta)$, and $BiI_3(\beta)$ by eq 1. These are shown in Table I. The volume of the solid phase at the melting point was computed from density data of Cubicciotti, et al.,[27-29] and from the calculated values of ΔV_f, i.e., $V_{solid} = V_{liquid} - \Delta V_{fusion}$. The ratios of molar volumes of liquid and solid $BiCl_3$, $BiBr_3$, and BiI_3 at their normal melting points are shown in Table I. These ratios for the bismuth halides are comparable to the ratios obtained for typical salts such as the alkali halides.[31]

Melting curves have commonly been reported in the form of the Simon[32] equation

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