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The Electrical Resistivity of Solid and Liquid Tri-Iodides of Antimony and Bismuth

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(15. VIII. 1961)

Abstract: The electrical resistivities of SbI_3 and BiI_3 have been measured in their solid and liquid phases. The two compounds are found to be semiconductors with high resistivities at room temperature and high energy gaps. Semiconducting behaviour seems to persist in the liquid phases. The room temperature optical transmission has also been measured in the vicinity of the absorption edge.

1. Introduction

A great deal of attention has been given in recent years to compounds of the $A_2^{V}\,B_3^{VI}$ composition, particularly to those crystallizing in the rhombohedral C 33 structure, for example Bi_2Te_3. Compounds of the generic formula $A^{V}\,C_3^{VII}$ that crystallize in the trigonal DO_5 structure, for example BiI_3, have not so far been investigated with regard to their electrical properties. Discussing these DO_5 phases MOOSER and PEARSON[1]) predicted that they should be semiconductors. The present investigation, it will be seen, supports this conclusion for the antimony and bismuth iodides.

2. Experimental Method

The compounds were prepared by melting together stoichiometric amounts of the elements in evacuated and sealed silica tubes. After the melting, the tubes were slowly lowered out of the furnace, with the aim of segregating impurities or excessive amounts of either component. Large single crystals with typical layer structure were formed, from which it was easy to obtain thin plates suitable for optical investigation. The optical transmission was measured with a 112 U-Perkin Elmer spectrometer fitted with a fused silica prism; only the room temperature transmission was measured.

Because of the high volatility of iodine it was decided to seal the compounds into pyrex tubes to perform the electrical resistivity measurements. It was thus also possible to measure the resistivity in the liquid phase of these compounds. Pyrex tubes of 3 to 4 mm in diameter were cut into pieces of 1 to 3 cm in length. They were re-joined after a strip of platinum (10 microns thick and 1 mm wide) had been placed between them (see Fig. 1). A minimum of four such strips were fitted to a tube for resistance measurements to be made by a four probe method*). It was quite difficult to obtain vacuum tight seals because of the different thermal expansion of platinum and pyrex glass, and several tubes had to be rejected. The compounds were then cast into the tubes. After vacuum sealing, the tubes were again slowly lowered out of a furnace to produce segregation and large grains. The resistances were measured with two different bridges described elsewhere[2][3].

Since the iodine of the compounds studied reacts with platinum at temperatures much above room temperature it was necessary to perform measurements at such temperatures as rapidly as possible. On the original melting of the compounds into the pyrex tubes it was unavoidable that the substances became contaminated to some extent with platinum, which affected the results. For SbI_3, with its low melting point of 166° C, this effect is not very important, but becomes quite considerable for BiI_3, which melts at 397° C[4]. It is also worth noting that large thermoelectric voltages were observed in the two compounds; it was therefore necessary to place the samples in heavy copper jackets to make isothermal measurements possible.

3. Discussion of the Measurements and Results

In order to obtain results that would be affected as little as possible by the corrosion of the electrodes, two samples of BiI_3 were prepared. The first sample was used to measure the resistivity of the solid phase. It was heated slowly up to 360° C and then cooled (Fig. 1). The resistance measured on cooling was appreciably different from that measured on heating. On the second heating run with this sample the same results were obtained as during the previous cooling. The second sample was used to investigate the process of melting. It was first heated rapidly to 360° C with few readings taken. Then it was slowly cycled through the melting point. It is seen (on the insert of Fig. 1) that because of the large thermal capacity of the furnace and the latent heat of the sample an apparent hysteresis is observed; the furnace temperature continues to drift while the sample

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*) The strips were cut level with the glass on the inside of the tubes so that measurements of the Hall voltage could be performed; so far, however, we have not succeeded in measuring any Hall voltage.

remains at the melting point until all the substance has undergone the change of phase. It is also observed that with the steady increase in platinum content the melting extends over a wider range of temperatures, and the resistivity of the solid phase diminishes. The resistivity of the liquid phase appears to be insensitive to the platinum content.

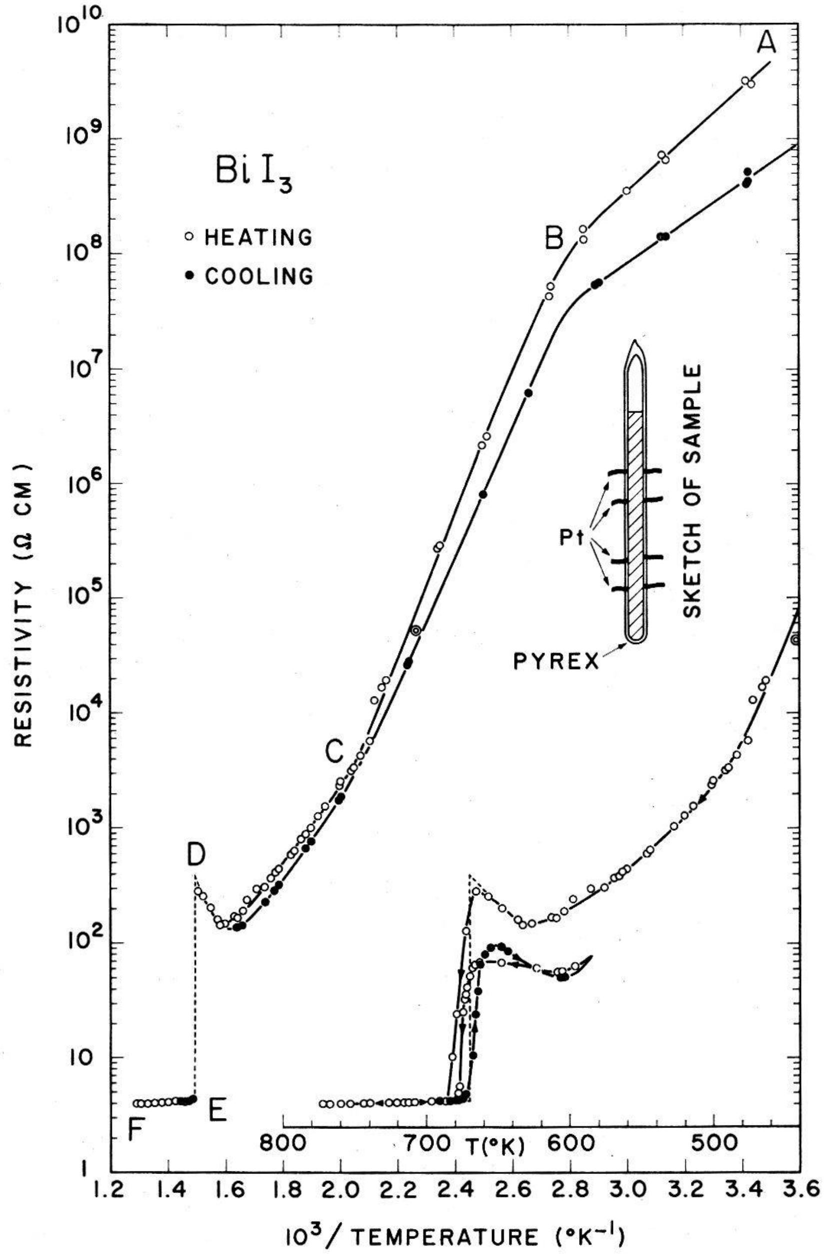

Fig. 1

Electrical resistivity of BiI_3 as a function of the inverse temperature. Note that the insert has the same ordinate but a linear temperature scale as abscissa.

Combining measurements from the two BiI_3 samples, one can expect to obtain the resistivity of uncontaminated BiI_3. The curve labelled 'heating' on the main graph of Figure 1 should give the resistivity of unspoiled

BiI_3. The curve labelled 'cooling' gives results on cooling from about 360° C and subsequent re-heating. The insert in Figure 1 shows in detail the measurements obtained on cycling several times through the melting point.

The curve attributed to unspoiled BiI_3 has several distinctive parts. Part AB most likely corresponds to an impurity range, with an activation energy of 0.88 ± 0.05 eV. Part BC, with an activation energy of $2.5_2 \pm 0.10$ eV, gives the intrinsic resistivity. The behaviour observed between C and D is quite unusual; it may result from pre-melting phenomena or decomposition; it is somewhat difficult to accept that pre-melting phenomena could be significant 180° C below the actual melting. The resistivity of the liquid phase (EF) is about 100 times smaller than that of the solid, and it continues to decrease with increasing temperature, yielding an activation energy of $0.06_3 \pm 0.010$ eV. We have not tried to determine whether there is an important ionic contribution to the conductivity of the liquid phase, but we believe that it is small, since there have been no signs of any sudden increase in the corrosion of the platinum electrodes.

SbI_3 behaves quite similarly to the bismuthide. The experiments are easier because of the lower melting point. The detailed measurements on cycling through the melting point, shown on the insert of Figure 2, indicate that corrosion of the platinum electrodes takes place at a much slower rate. Other striking differences that can be observed in Figure 2 are (1) the reproducibility of the measurements on heating and cooling several times; (2) the apparently very sharp onset of melting and solidification. One should note, in particular, that on the initial heating and cooling runs melting started at exactly the same temperature as solidification; (3) the absence of any pre-melting effects similar to those observed in the bismuthide, and (4) a very large dicontinuous increase in conductivity upon melting, by a factor of 450. Parts AB and BC are probably both typical of intrinsic behaviour, the small difference in slope may result from changes in the mobility of the charge carriers. The two activation energies derived below the melting point are 0.96 ± 0.05 and 1.16 ± 0.05 eV. In the melt (DE) the activation energy is 0.20 ± 0.05 eV.

Before concluding this discussion of the resistivity measurements we would like to point out that layer structures like BiI_3 and SbI_3 very likely have a highly anisotropic resistivity. We believe that the resistivity within one layer ($\perp$ to *c*-axis) is probably orders of magnitude smaller than the resistivity across the layer (// to *c*-axis). Since our measurements were performed on aggregates of large intertwined single crystals with their *c*-axes preferentially aligned at right angles to the sample axis, we think that our measurements give essentially the resistivity component perpendicular to the *c*-axis.

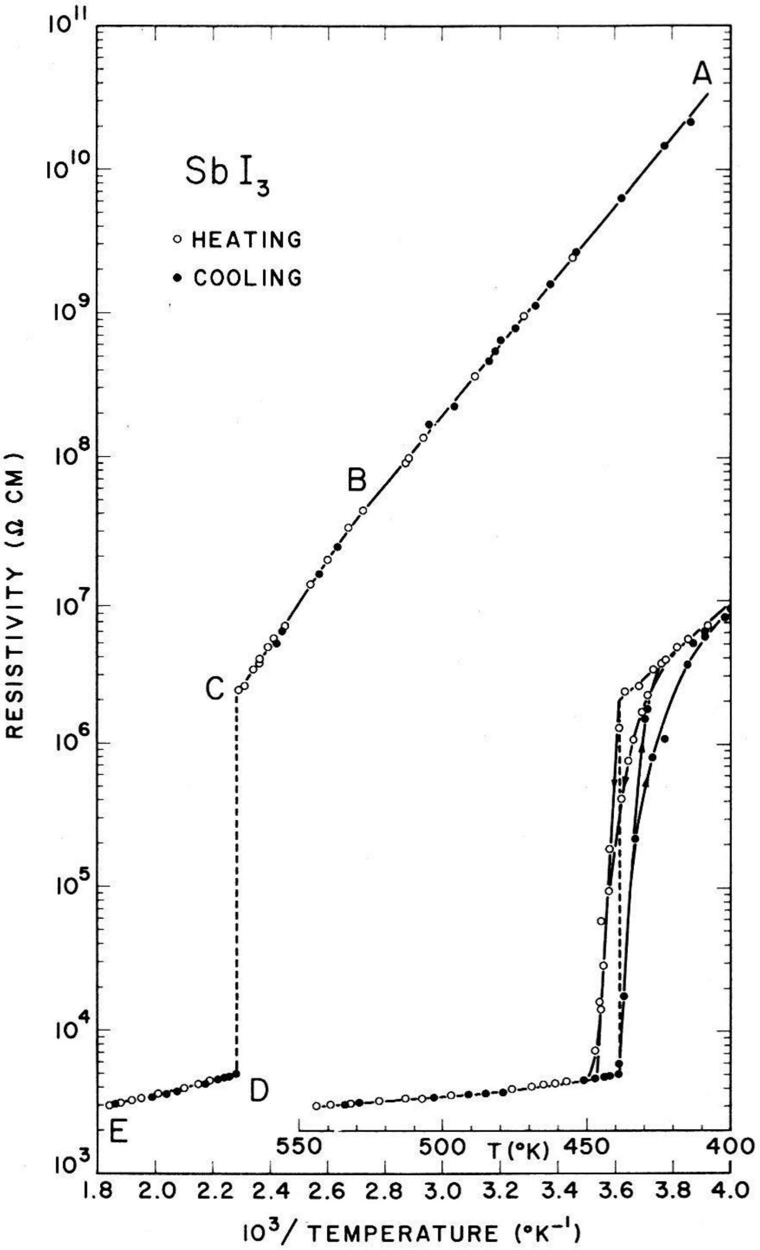

Fig. 2

Electrical resistivity of SbI_3 as a function of the inverse temperature. Note that the insert has the same ordinate but a linear temperature scale as abscissa.

With a view to obtaining more information on the intrinsic activation energies, the room temperature optical transmission of two thin plates has been measured. The results displayed in Figure 3 show absorption edges at energies of 1.81 ± 0.02 eV for BiI_3 and 2.12 ± 0.02 eV for SbI_3 at 295° K. The comparatively high absorption of BiI_3 probably arises through direct optical transitions from the maximum of the valence band to the minimum of the conduction band. The optical absorption edge would therefore correspond to the energy gap. If one assumes purely thermal scattering, the intrinsic activation energy derived from resistivity measurements corresponds to the energy gap at the absolute zero of temperature. The data obtained for BiI_3 indicate a large variation of the energy gap, from 2.52 eV at 0° K to 1.81 eV at 295° K. An investigation of the optical absorption and luminescence of BiI_3 at 77° K has recently been made in Russia[5]); at that temperature the absorption edge lies at 2.02 eV. One must therefore conclude that the temperature dependence of the energy gap is highly non-linear.

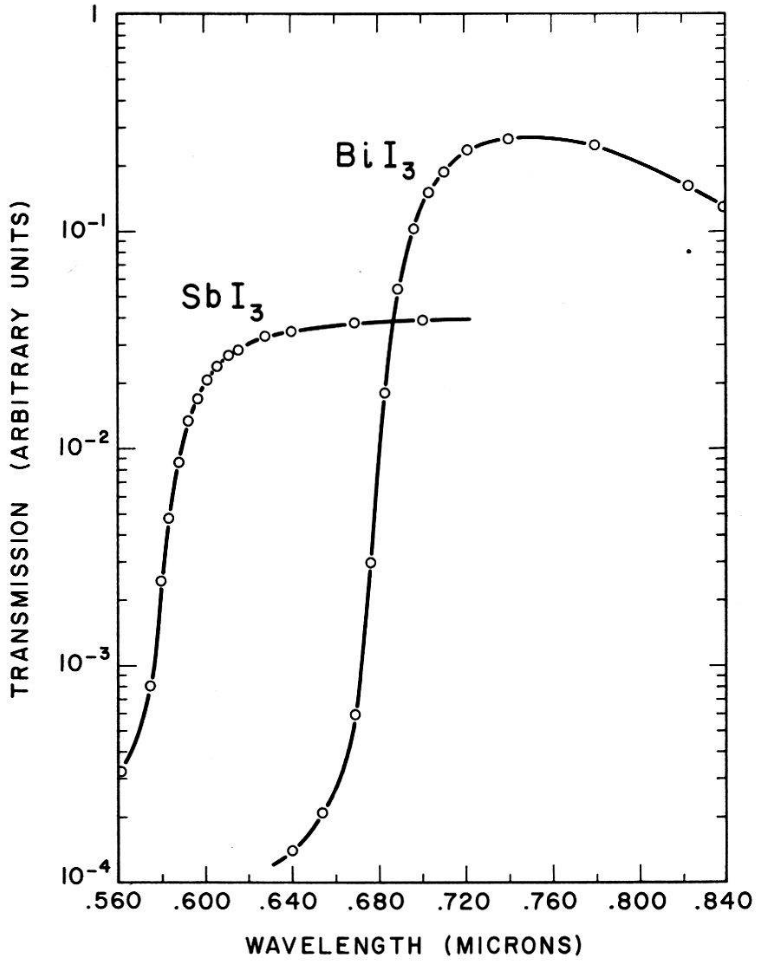

Fig. 3

Optical transmission of a sample of BiI_3 (about 40 microns thick) and a sample of SbI_3 (about 200 microns thick). The values of the transmission of SbI_3 are to be multiplied by ten.

The data obtained for SbI_3 cannot be interpreted in the same manner since the optical absorption is very much weaker and the edge does not seem to correspond to the energy gap. The findings could be understood if the maximum of the valence band was not lying at the same point in the reduced Brillouin zone as the minimum of the conduction band. The direct optical transitions would involve a larger energy than the thermal activation of carriers.

For convenience we have collected the main parameters discussed here into the Table.

	E_g solid phase, in eV at 0° K	ΔE liquid phase, in eV	Optical absorption edge, in eV		Resistivity at the melting point, in $\Omega \cdot$ cm	
			295° K	77° K	solid	liquid
BiI_3	$2.5_2 \pm 0.10$	$0.06_3 \pm 0.010$	1.81 ± 0.02	2.02 5)	~ 400	4.2
SbI_3	$0.96\text{–}1.16 \pm 0.05$	0.20 ± 0.05	2.12 ± 0.02		2.2×10^6	4.9×10^3

4. Conclusion

It has been established that BiI_3 and SbI_3 are semiconductors with high intrinsic resistivities and large energy gaps. It seems that the two compounds still exhibit semiconducting properties in the liquid phase, although ionic conductivity has not been completely ruled out.

5. Acknowledgements

We wish to thank Dr. W. B. Pearson for interesting discussions.

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