lines in this figure are the heating curves at constant load. It is to be noted that we clearly observed the II′ phase as reported by Tikhomirova *et al.* (1966). All the phase lines shown are for the transition as it first takes place upon increasing the temperature across the phase boundary.

In the second type of experiment, in which we compared the phase diagram of bismuth against the melting curve of mercury, we again obtained $\Delta P/\Delta T = 0 \cdot 016$ kbar K^{-1} below 30 kbar where the phase changes of these materials are accurately known. If we again assume the same value at higher pressures we reproduce the same phase diagram for bismuth as shown in figure 6. The Bi II′ phase was again observed and the Bi II–II′ transition signal is shown in figure 4a. The other transitions of bismuth shown in figures 4 and 5 are near various triple points. For these measurements we assumed the melting curve of mercury of Bogdanov *et al.* (1971) to be accurate to 30 kbar and used their extrapolation to 50 kbar.

Once we had a value for $\Delta P/\Delta T$, we measured the phase diagrams for lead, thallium, tin, indium, and mercury to check the consistency of our results. In figures 7 and 8 we show the phase diagrams for these materials. The Tl I–II phase line was not observed for it was so steep that no latent-heat signal appeared upon heating through this region.

4 Discussion and conclusions

Pressures calculated from the melting curve of mercury of Bogdanov *et al.* (1971) are estimated to be accurate to ±0·5% between 10 and 30 kbar, and in the extrapolation from 30 to 40 kbar accurate to ±1%. The only other measurements of the melting curve of mercury above 30 kbar are those of Klement *et al.* (1963a), which agree to within 0·1 kbar with those of Bogdanov *et al.* to 30 kbar, but are higher in pressure than the extrapolation of Bogdanov *et al.* by 1·5 kbar at 40 kbar and 6 kbar at 55 kbar. This discrepancy is considerably larger than the uncertainty estimated by these authors. The pressures estimated at Kennedy's laboratory at that time, however, were likely to be too high as was noted in the results for bismuth reported above. Thus the pressure at the melting curve of mercury is not as well known as we would desire for this work.

The only other measurement of the Hg II–I phase line is by Klement *et al.* (1963a), and their results are consistently 3 K below ours. Their measurements were, however, taken as the average of the signals upon increasing and decreasing the temperature through the phase lines. They observed 6 K hysteresis at 42 kbar. Our results are taken at the II–I phase change on increasing temperature. This choice was made because of the shape of the DTA signals which indicated this transition to be much nearer the equilibrium conditions for the transition. (Note the large supercooling effects observed for the II–I transition in figure 3b.) These measurements and those of Klement *et al.* are thus in extremely good agreement. If we had used their melting curve of mercury for our calibration rather than the extrapolation of Bogdanov *et al.*, we would have had a 5·6 kbar disagreement with the Hg II–I line of Klement *et al.* near 50 kbar. This is an indication of a discrepancy between the pressure measured by Klement *et al.* near room temperature and those measured at higher temperatures at these pressures, or of an error in our $\Delta P/\Delta T$. The latter would require a value of 7·2 kbar/100 K which is completely impossible when considering the rest of our data.

The melting curve of indium runs nearly parallel to the melting curve of mercury and is 170 K above it. The pressure correction due to heating above the mercury calibration would thus be 2·7 kbar all along the curve. The measured melting line is in good agreement with the one reported by Millet (1968) but is 1 kbar below that of Jayaraman *et al.* (1963) at 20 kbar and 6 kbar below their value at 50 kbar. Our results for indium, however, may be too high in temperature because the solidification signal always came at a higher temperature than the melting signal which showed a slight rounding. These effects indicate a possible alloying, so this curve could be as much as 10 K too high at the largest pressures.

The melting curve of lead is 2·5 kbar lower than the measurements of Akella *et al.* (1973) at 50 kbar and 1 kbar below theirs at 25 kbar. Our results are about 1 kbar above those of Millet (1968) in this same range. Again, as with indium, we found some rounding in the melting signal and a tendency for the solidification points to lie at higher temperatures than the melting points; thus our results may have an uncertainty as large as 2 kbar at the highest pressure point. If we used the melting curve of mercury due to Klement *et al.* (1963a), however, rather than the extrapolation of Bogdanov *et al.* (1971) for our pressure standard we would find our pressures to be 1·5 kbar above those of Akella *et al.* at the highest points. The parameter $\Delta P/\Delta T$ must be $1{\cdot}6 \pm 0{\cdot}2$ kbar/100 K for our liquid cell in order to get any reasonable agreement between our results and those of Akella, confirming our measurement of this parameter.

The phase diagram of thallium agrees well with that of Jayaraman *et al.* (1963) to the triple point, but their pressures are 2 kbar higher than ours at 50 kbar along with the III–I phase line. We chose the equilibrium values for the transitions as midway between the up and down transitions which showed considerable hysteresis, especially near the triple point. This choice is motivated by the symmetrical shape of the transitions shown in figure 9a. Our II–I phase line shows more curvature than that of Jayaraman *et al.* We measured $(\mathrm{d}T/\mathrm{d}P)_{\mathrm{II-I}} = -4{\cdot}4\ \mathrm{K\ kbar^{-1}}$ and $(\mathrm{d}T/\mathrm{d}P)_{\mathrm{III-I}} = +17\ \mathrm{K\ kbar^{-1}}$ at the triple point. The latent heat signals were about equal; using the values of ΔV measured by Jayaraman *et al.* we found them to be $\Delta H_{\mathrm{II-I}} = 0{\cdot}19\ \mathrm{cal\ g^{-1}}$ and $\Delta H_{\mathrm{III-I}} = 0{\cdot}24\ \mathrm{cal\ g^{-1}}$, respectively, leaving $\Delta H_{\mathrm{II-III}} = 0{\cdot}05 \pm 0{\cdot}05\ \mathrm{cal\ g^{-1}}$. The fact that no latent heat signal was observed for the II–III transition indicates that $\Delta H_{\mathrm{II-III}} \lesssim 0{\cdot}02\ \mathrm{cal\ g^{-1}}$, and the slope of the II–III phase line is steeper than 240 K kbar^{-1}, but the sign of the slope is not determined. Bridgman's (1935) volume measurement between phases I and II appear unreliable.

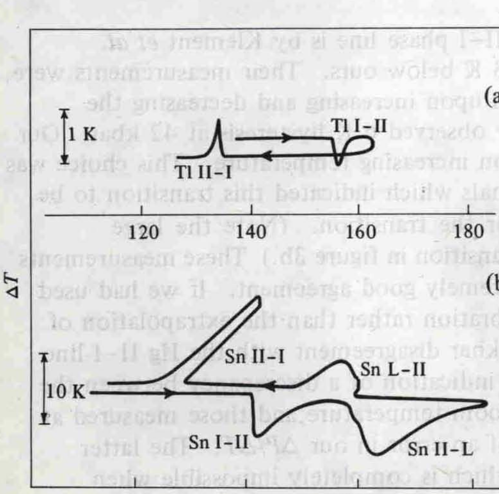

Figure 9. (a) DTA signals for the Tl III–I transition on increasing and decreasing temperature. (b) DTA signals for the Sn II–I melting transitions.