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► **To cite this version:**

Karim Khalouk, Moussa Mayoufi, Jean-Georges Gasser. Are there phase transitions in liquid metallic alloys?. *Philosophical Magazine*, 2010, 90 (20), pp.2695-2709. 10.1080/14786431003745310. hal-00596602

HAL Id: hal-00596602

<https://hal.science/hal-00596602>

Submitted on 28 May 2011

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|-------------------------------|--|
| Journal: | <i>Philosophical Magazine & Philosophical Magazine Letters</i> |
| Manuscript ID: | TPHM-09-Dec-0514.R1 |
| Journal Selection: | Philosophical Magazine |
| Date Submitted by the Author: | 14-Feb-2010 |
| Complete List of Authors: | KHALOUK, Karim; Université Paul Verlaine - Metz, Laboratoire de Physique des Milieux Denses Mayoufi, Moussa; Université d'Annaba, Chimie Gasser, Jean-Georges; Université Paul Verlaine - Metz, Laboratoire de Physique des Milieux Denses |
| Keywords: | phase transitions, liquid alloys, liquid metals, resistivity |
| Keywords (user supplied): | |
| | |



Are there phase transitions in liquid metallic alloys?

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Keywords Liquid metallic alloys, resistivity, phase transitions, anomalies, indium, bismuth, lead, liquid phase.

Abstract. Recently, resistivity measurements of some liquid metals and metallic alloys have been published using an electrode technique. A marked change of the slope of the resistivity versus temperature has been observed following the history of the alloy in the liquid state and the authors conclude to “*structural transitions in the melt*”. It is interesting to examine such effects and to try to understand their origin. In this work, the resistivities of several liquid **metals** and metallic alloys have been measured as function of temperature. A particular attention has been given to the history of the alloy including solidification and melting conditions. We also observed “*anomalies*”. Our experiments lead us to conclude that they must very probably be attributed to the release of gas or vapour bubbles in the liquid alloy at the first heating resulting from a decomposition of compounds like oxides or hydroxides of the metals not from a phase transition in the liquid metallic state like “*breaking*” Sn-Sn covalent bands.

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1. Introduction.

Xi et al. [1] measured six different compositions of liquid Bi-In alloys between the melting point and 1000°C. They observed a drastic change of the temperature coefficient of the resistivity of four alloys, the most important was observed for $\text{Bi}_{52.73}\text{In}_{47.27}$ at%². The authors suggest a significant change of the short range order in different Bi-In melts. Yu et al. [2] measured seven different compositions of liquid In-Pb between the melting point and 1200°C. A marked turning point on resistivity-temperature curve was observed far above the liquidus mainly for the $\text{In}_{75.54}\text{Pb}_{24.46}$ en atomic% corresponding to $\text{In}_{63}\text{Pb}_{37}$ in weight%. They also suggest a structural transition of these melts like other authors [3, 4, 5, 6, and 7] of the same laboratory who have observed the same phenomena for several other binary alloys. However, Jia et al. [8] did not observe this phenomenon but their experimental process is different and is more like our earlier experiments i.e. they (and we) did not consider as correct the first heating measurements. Having developed since many years an experimental design (cell(s) + measurement methods) able to make accurate resistivity measurements, we feel necessary to check if we observe the same behaviour as that reported by Xi et al. [1] and Yu et al. [2] and others [3 to 7] by using our experimental cell and the same experimental process than the Hefei's group.

From a physical point of view two kinds of phase transitions have even been encountered in liquid alloys. The first one concerns the demixtion of some metallic or semi conducting alloys, the second one concerns metallization of liquid semiconductors by increasing temperature. From a quantum mechanics point of view the demixtion is induced by the difference between homo and hetero coordination characterised by the difference of pair potentials. The semi conducting to metallic transition is characterised by breaking covalent bonds with temperature, changing drastically the short range order and the number of nearest neighbours (from 2-3 to 8-11). This corresponds to the transition from a semiconductor like density of states (with a band gap) to a metallic one by reducing and by filling this band gap. Semi conductor behaviour appears in some II-VI (like Cd-Te or Zn-Te) , III-V (Al-Sb), II-V (Cd-Sb, Zn-Sb) III-VI (Tl-Te) etc which are semi conductors in the solid state. The resistivity varies in the range from about 100,000 $\mu\Omega\cdot\text{cm}$ to 200 $\mu\Omega\cdot\text{cm}$ and the breaking of the bonds

² All concentrations are given in atomic %. The values in the literature given in mass% have been converted to atomic%.

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3 corresponds to an important negative temperature coefficient of the resistivity (typically more
4 than ten to hundred times the value of metallic systems). Taking into account the order of
5 magnitude of the resistivities, the alloys studied by the Hefei's group have a purely metallic
6 behaviour and are metallic in the solid state. Their anomalous behaviour is different from the
7 two ones described above.
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14 When one is making molecular dynamics simulation under the effect of metallic potentials,
15 the atomic configuration changes completely every 10^{-13} to 10^{-12} seconds. A resistivity
16 measurement takes about 10^{-2} to 1 second. This means that during the resistivity experiment,
17 the atomic configuration has changed 10^{10} times or more. The observed phenomena are
18 difficult to understand from a statistical mechanics point of view with classical metallic
19 potentials with a first minimum and with Friedel oscillations. However one can find a
20 theoretical explanation of the observed measurements. It is possible to imagine an interatomic
21 potential presenting two minima, one deeper than the other. Just after melting, the atomic
22 distance corresponds to a first minimum heritated from the solid configuration, something like
23 a bond. When heated above a given temperature, the kinetic energy is sufficient to allow the
24 atoms to jump into the deepest minimum from where it is not possible to come back in the
25 first minimum. So it is interesting to examine carefully the experimental results of these
26 alloys in order to check if such a mechanism is possible.
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39 We often encountered difficulties to get a stable value of the resistivity of liquid alloys in the
40 first heating curve and observed marked deviations from the expected curve. The question
41 arises if such behaviour may be explained by purely experimental problems or if we must
42 invoke a new physical phenomenon. The object of this work is to arbitrate between a "*phase*
43 *transition*" in the liquid state as claimed by ref [1] to [7] and experimental phenomena like
44 liquid concentration homogeneity or/and release of bubbles.... Among the different possible
45 experimental problems, the most encountered is the release of gases which can be dissolved
46 or/and adsorbed or/and resulting from an oxide or hydroxide decomposition or/and of bubbles
47 due to the vapour pressure of the metals itself when approaching their boiling point. The
48 chemical inhomogeneity of the liquid alloy at the expected concentration in the measurement
49 capillary can also explain measurement errors. Our experimental design permits us to mix
50 mechanically the alloy allowing us to homogenise it, to remove bubbles by pumping or to
51 reduce their size by increasing argon pressure. After these operations and thermal cycles, the
52 resistivity is stabilized on a reproducible curve and is independent of the argon pressure up to
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6 bars which means that either argon does not dissolve in the liquid alloy or if it dissolves, it has no effect on the resistivity. The uncertainty on the measured resistivity is better than 0.4%; that on concentration is better than 0.3%; that on temperature is better than 0.4%. In §2 we present our measurement method and describe our experimental device. In §3 we report and discuss our experimental results. We realize our measurements for three compositions of the Bi-In alloy and for one composition of the In-Pb alloy. Then we examine the behaviour of the three pure metals: bismuth, indium and lead. Then we conclude.

2. Experimental method.

The liquid alloy is contained in a quartz cell (figure 1). This cell has already been described [9]. It allows us to measure the resistivity from the liquidus to 1250°C. The electrical resistivity is measured with a four probes DC technique. The resistance of an arbitrary shape capillary is given by:

$$R = \int_0^L \rho \frac{dl}{S(l)} .$$

where ρ is the resistivity (temperature and concentration dependent), dl is an element of length of the capillary and $S(l)$ is the section of this element of length. At constant temperature and concentration (non uniform temperature and concentration induce errors in the measurements), the resistivity is independent from the position l , thus: $R = \rho \int_0^L \frac{dl}{S(l)} = \rho \cdot C$.

The integral C is a pure geometric constant characteristic of the cell that we call the “constant of the cell”. This constant is measured with tri-distilled mercury at room temperature (the resistivity of mercury at room temperature is well known [10]). The electrodes are in tungsten and they are sealed in quartz. The temperature is measured with three external K-type thermocouples. The cell is placed in the most temperature homogenous part of the furnace.

It is first absolutely necessary to describe completely and accurately the experimental protocol in order to be able to understand and explain the observed phenomena. A solid ingot of the alloy is pre-melted in a quartz tube and can be heated at different temperatures (just above the liquidus or at several hundreds of degrees). The ingot is introduced in the measurement cell (figure 1), heated under vacuum, re-melted and pushed into the capillary by argon pressure. The resistivity had been measured from the melting point to 1100°C for all alloys, both by

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3 increasing then by decreasing temperature several times. The heating and cooling rate is
4 between 0.5 and 2°C per minute in order to be always in thermal equilibrium between the cell
5 and the furnace (quasistatic regime).
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10 **3. Discussion and results.**

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13 To compare our results with Xi et al. [1] and Yu et al. [2], we try to reproduce **their**
14 **experiments by using the same** experimental method and process. Our alloys were prepared at
15 the expected composition from pure elements (purity: 99.999% for In, Bi and Pb), melted
16 under vacuum in a quartz tube, heated, shocked, then cooled rapidly at room temperature
17 under argon pressure in order to get an alloy “as concentration homogenous” as possible. The
18 ingot is then placed into the resistivity measurement cell, re-melted under vacuum, and
19 pushed into the measurement capillary by applying pressure which can be increased up to 4
20 bar relative to atmosphere. The homogeneity of the liquid alloy is obtained by mixing it
21 “mechanically” five to ten times by applying successively vacuum and pressure before
22 beginning any measurement.
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33 **3.1. Experiments on Bi_{52.73}In_{47.27} (in atomic %).**

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36 We reproduce on figure 2 four measurements that we obtained successively and compared
37 with the electrical resistivity of Xi et al. [1]. Arrows indicate that we either apply vacuum to
38 empty the capillary or increase the pressure to decrease the size of bubbles (if present in the
39 capillary). In the first heating we melt the alloy at 180°C. We empty and fill the capillary
40 several times thus mixing mechanically the liquid alloy. **At our concentration, the alloy, if**
41 **homogenous, must be liquid above 110°C. The temperature is 70°C above the liquidus and**
42 **21°C above the indium melting temperature.** We then heat it at 300°C measuring the
43 resistivity. At this temperature we are above the whole liquidus curve **(particularly we are**
44 **above the melting point of pure bismuth 271.4°C which is the highest temperature of the**
45 **liquidus curve).** Thus we are sure that all grains are melted. We empty the capillary and mix
46 several times the liquid applying always the same pressure (+ 0.5 bars relative to atmosphere
47 and +1.5 bars in absolute). We observe a small decrease of resistivity. This is a proof that the
48 liquid in the capillary was not exactly at the nominal composition, despite the fact that the
49 alloy liquidus is **at** 110°C. We continue to heat up to 800°C under 1.5 bar (absolute) argon
50 pressure where Xi et al. [1] observed a change of slope (they did not indicate at what pressure
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3 they work). We also observe a similar but much less marked phenomenon. At this
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5 temperature we increase the pressure from 1.5 bar to 2 bar then to 2.5 bar. We observe a
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7 decrease of the apparent resistivity. This operation is repeated at 950°C where the same
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9 behaviour is observed. We link this observation to the presence of bubbles in the liquid
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11 (which change a little the geometrical constant C of the electricity conducting liquid column)
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13 that an increase of argon pressure reduces. Afterward, we decrease the temperature from
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15 1100°C to 180°C without changing anything (second curve indicated first cooling on figure
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17 2). At this temperature the resistivity is nearly the same as at the beginning of the experiment.
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19 We empty and fill several times the capillary, then we make a second heating and cooling
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21 resistivity measurement under 1.5 bar (absolute scale). We no more observe any anomaly in
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23 the second heating and second cooling which are superposed. This is coherent with Xi et al.
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25 [1] observations. When we compare the first heating curve to the stable curve we can observe
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27 that the phenomenon begins slowly above 400°C while Xi observed a rapid variation near
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29 700°C, but the applied pressure is not given by these authors.

30 **3.2. Experiments on Bi₈₀In₂₀ (in atomic %).**

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33 For this concentration, no resistivity measurement has been published to our knowledge. In
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35 this experiment (figure 3), the alloy was prepared at 280°C, introduced and melted in the
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37 measurement cell. We heated and mixed the alloy in a quartz tube at 280°C, which is above
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39 the highest temperature of the liquidus curve, and then we cool it. The ingot is introduced in
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41 the measurement cell and is heated. Near 850°C, we observe an inflexion of the resistivity
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43 curve which is also represented on an expanded scale (figure 4). Near 900°C the resistivity
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45 began to diverge. Near 980°C we increase the pressure from 1.5 to 2 bar (absolute).
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47 Immediately the apparent resistivity decreases from 181.7 to 170.6 $\mu\Omega.cm$. A second
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49 increases to 2.5 bar brings the resistivity at 162.5 $\mu\Omega.cm$. We then cool the alloy (first cooling
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51 curve). At 280°C (figure 3), we empty and fill several times the capillary then we heat and
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53 cool again the alloy. The second heating and cooling curves (at 1.5 bar) are very near, and we
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55 no more observe the change of slope of the resistivity above 850°C (figure 4). Comparing the
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57 first heating to the stable curve we can observe that the phenomenon begins above 850°C.
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3.3. Experiments on Bi₂₀In₈₀ (in atomic %).

Two different experiments have been done for this composition.

- In the first one (sample 1), we have first heated the melt up to 1000°C under argon pressure. We outgassed the liquid alloy, from time to time we applied very rapidly (in order to avoid any distillation) the vacuum then we cool the sample and solidify it at room temperature. The ingot stayed in air several hours. The prepared ingot was introduced and melted again in the measurement cell. Figure 5 shows resistivity versus temperature measurement. With this ingot, the resistivity increases abruptly at a higher temperature (near 950°C only). We apply vacuum for a few seconds and applied again the same argon pressure. Immediately the apparent resistivity decrease from 94 to 87 $\mu\Omega.cm$. The first cooling and the second heating and cooling curves are exactly superposed. Comparing the first heating to the stable curve we can observe that the phenomenon begins slightly above 900°C and becomes important near 950°C.
- In the second experiment (sample 2) (figure 6), we have heated the prepared alloy in the measurement cell itself placed in a horizontal position in order to liberate more easily the gas bubble which can be present in the measurement capillary. We have solidified the ingot in the cell always protected by vacuum or by argon. **The ingot has never been put in contact with air.** Figure 6 shows that the curve of resistivity as function of temperature is linear and that the first heating curve and the first cooling one.

We concluded that the presence of air (or/and moisture) on the solid ingot is necessary to obtain the anomalous behaviour described.

3.4. Experiment on In_{75.54}Pb_{24.46} (in atomic %).

- The alloy was prepared at 350°C (sample 1). Above this temperature we are sure that all grains of pure metals are melted since we are above the melting point of lead (324°C). We mix mechanically the alloys by applying pressure and vacuum several times. After this operation we cool rapidly the alloys and put it into the resistivity cell. On figure 7 we present the measurements of resistivity versus

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3 temperature. From 600 to 725°C the resistivity of the alloy increases rapidly and
4 the increase of pressure is not sufficient to reduce it. So we applied vacuum for a
5 few seconds. The resistivity decreases immediately from 69.3 to 61.1 $\mu\Omega.cm$. This
6 indicates that the release of gas is probably much more important than for
7 $Bi_{67.72}In_{31.27}$. At 990°C the same behaviour is observed and vacuum is applied
8 again for a few seconds. The resistivity curve became then stable and the cooling
9 curve is linear. Comparing the first heating to the stable curve we can observe that
10 the phenomenon begins first above 600°C then again near 900°C. Only the second
11 effect has been observed by Yu et al [2].

- 12 • On figure 8 we present a second experiment (sample 2) at the same composition.
13 The resistivity diverges at 950°C (300°C above sample 1) but the departure from
14 the linear curve begins near 800°C. We try first to increase the pressure but this
15 operation has no effect. We apply vacuum for a few seconds and observe that the
16 apparent resistivity now decreases and falls on the extrapolation of the low
17 temperature curve. We continue to heat the alloy under 1.5 bar and observe again
18 an anomalous behaviour; we consider that a change of pressure is necessary again.
19 We increase the pressure up to 3 bar at 1050°C and immediately the resistivity
20 decrease from 76.2 to 74.6 $\mu\Omega.cm$. The effect is to decrease again the resistivity
21 which increases nearly linearly up to 1100°C. We then cool the sample. At 820°C
22 we decrease the pressure from 3 to 2 bar. A very slight increase is observed. This
23 is the proof that a very small bubble expands.

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25 We are convinced that application of vacuum during a longer time would have evacuated all
26 gases. However our experience on liquid alloys hints us to apply vacuum during a too long
27 time at high temperature because of evaporation of the component having the highest vapour
28 pressure. Indeed this effect would change concentration of the liquid alloy. In our
29 experiments, we are sure that no metal evaporation occurred.

30 **3.5. Experiments on pure metals.**

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32 The phenomenon observed by ref 1 to 7 has not been reported for pure metals. Thus we feel
33 necessary to measure also the resistivity of the three pure metals used in our alloys. Our
34 measurements are reported on figure 9 for bismuth, on figure 10 for lead and on figure 11 for
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indium. The phenomenon observed for alloys appears also in pure elements. It is observed first between 400-500°C for bismuth then again between 800 and 900°C. For pure lead we first observe a slight phenomenon between 500-600°C characterised by a higher dispersion of the experimental points. Above 900°C, lead presents a sharp variation of its apparent resistivity. For pure indium measurements are difficult between 450 and 700°C. Once heated at high temperature, this phenomenon disappears for the three pure elements. The variation in alloys corresponds roughly to those observed in the same temperature domain for the two pure elements. On figure 2 the anomaly can be clearly attributed to bismuth and indium. In the indium rich alloy studied (fig 3, 4, 5) only the second deviation of bismuth near 900°C seems to appear. For indium-lead (fig 7 and 8) the anomaly near 600°C can be attributed to indium while that near 900°C may correspond to lead.

Our conclusion is that applying pressure or vacuum removes existing bubbles in the liquid metal as for alloys whatever their origin is. A second observation is that Xi et al. [1] and Yu et al. [2] are far from our measurements (nearly 10% below our curves). Thus we have also reported on figures 9, 10 and 11 experimental results of other authors [11, 12, 13, 14, 15, 16, 17, 18] which are near our values. Such a systematic difference is generally due to the calibration of the constant of the cell.

3.6. Influence of time.

We will now discuss another experimental procedure tested on Bi₃₀In₇₀ (atomic %). We start by measuring the resistivity of pure bismuth, several times up to 1000°C. We then added pure indium grains in the primary storage tank (figure 1). The alloy is thoroughly mechanically mixed. The first heating starts at hour H with 91.67 μΩ·cm at 180°C (figure 12, upper curve). No anomaly is observed up to 1000°C, the first cooling (beginning at time H+15) is a little below. At 180°C the resistivity (89.13 μΩ·cm) is 2.5 μΩ·cm below the departure. We then empty and fill several times the capillary and obtain a stable resistivity of 82 μΩ·cm which has even be lowered of 7.1 μΩ·cm below the value indicated in our first run (89.13 μΩ·cm) We heat again (hour H+30) the alloy to 1000°C and cool it; the second cooling curve (hour H+45) is a little lower than the second heating one. The resistivity (at hour H+60) obtained at 180°C is 81.16 μΩ·cm. At this temperature we mix the alloy again, the resistivity decreases to 78.4 μΩ·cm. Our third heating (hour H+75) and cooling curves are now superimposed. We

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3 empty and fill again the capillary. Our forth heating and cooling curves **beginning at H+90**
4 **and ending at H+120** are exactly on the third heating and cooling curves. This last
5 measurement is that we admit as exact. This experiment shows that it is not easy to mix a less
6 dense metal like indium to a denser one which is at the bottom of the measurement cell when
7 indium is introduced. It has not been reported that Bi-In has tendency to homocoordination.
8 Figure 12 shows that density differences **prevent** a rapid mixing of liquid metallic alloys since
9 it was necessary to wait several days and to heat 700°C above the melting point of the
10 elements to obtain a macroscopic homogeneous liquid alloy characterised by a stable
11 resistivity.
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4. Conclusions.

- 1) Many anomalies have been observed in the curve of resistivity versus temperature both in the pure metals (that has never been reported) and in alloys. A change of the slope of the apparent resistivity occurs on all the first heating curves like observed by ref [1] to [7]. Even taking high purity metals gives rise to phenomena that we attributed to gases. But the nominal purity never includes oxides. It is possible that metals staying a more or less long time at room temperature can adsorb the gases and the moisture of the atmosphere. Solid compounds like oxides or hydroxides can be created and it is possible that they decompose near the temperatures where the resistivity changes have been observed. The releasing of gas influences then strongly the resistance measurement. The concept of our cell permits us to control and prevent bubbles formation in the liquid alloys by pumping to remove them or by applying an argon pressure to reduce their size. After these operations we have no more observed any anomaly. The sample solidified and **remelted** under argon pressure does not show this behaviour, confirming our hypothesis that the observed phenomenon is due to the gases of atmosphere (like oxygen or moisture) adsorbed or chemically linked to the metal.
- 2) Due to the gravity, it is difficult to mix (in a vertical capillary) metals with very different densities like bismuth and lead with indium. More, some alloys can present preference to homocoordination which **prevents a rapid** homogenization. We observed, for the first time to our knowledge, that some alloys **need more than one week to become homogeneous**. We have also observed that we more rapidly obtain a homogeneous alloy when we add, in the main tube and so in the capillary measurement tube, the highest density metal to the lowest one. Here the density difference helps mixing. The time necessary to homogenise the prepared alloys of different densities can also explain some change of the slope of the resistivity versus temperature. For these metals, it is both necessary to mix mechanically and to realize thermal cycles in order to ensure the homogeneity of the alloy.
- 3) It is not possible to conclude that preparing an alloy before the experiment and cooling it ensures that the reheated and re-melted alloy is homogenous. **Solidification gives grains of different solid phases with different concentrations and different melting points. Immediately after remelting, the liquid phase is**

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3 strongly heterogeneous and takes time to be mixed homogeneously. We are sure
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5 that all grains are melted only when the temperature is higher than the highest
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7 liquidus temperature (i.e. the melting point of pure bismuth in Bi-In alloys and of
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9 pure lead in In-Pb alloys).

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12 In the alloys studied in this paper and appealing to our experience of about 100 alloys studied
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14 in our laboratory, we many times observe the effect of pressure and vacuum. It has been
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16 clearly shown in this work, that the existing phenomena are strongly perturbed by applying
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18 pressure and/or vacuum.

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21 We are more convinced by a release of gas rather than by a phase transition in liquid metallic
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23 alloys. We have even visually, looking inside the furnace, observed the breaking of the
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25 conduction liquid column when we do not stop the evolution by pressure or vacuum. The
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27 decomposition temperature of a compound (oxide, hydroxide or other) is nearly in the same
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29 temperature range for pure metals and alloys. For alloys we can observe two temperature
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31 regions where this is observed, corresponding to the two elements. Other authors have
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33 discussed anomalies in the liquid state and their effect on the solidified alloys (Dahlborg et al.
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35 [19], Mhiaoui et al. [20]). They demonstrate that the scientific and technological problematic
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37 is important since the solids obtained can be different following the history of the melt. So it
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39 is certain that some effects exist and we suggest one plausible explanation in this paper.
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41 Before concluding to liquid-liquid transitions in metallic alloys by resistivity measurements, it
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43 is necessary to verify if all other reasons developed in our paper are excluded. Other
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45 experiments have been invoked by reference 1 to 7 (like DSC or internal friction) but all of
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47 them can also be explained by the explanation given in this paper i.e. by the release of gases.
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6 Figure 1: Quartz cell for resistivity measurements. The resistivity is measured by four
7 tungsten electrodes. Temperature is measured outside using three K-type thermocouples. The
8 concentration of the alloy can be changed by staying in the liquid state.
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11 Figure 2: Resistivity of $\text{Bi}_{52.73}\text{In}_{47.27}$ (atomic %) as function of temperature. Our
12 measurements compared to those of Xi et al. [1] obtained by digitalization.
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15 Figure 3: Resistivity of $\text{Bi}_{80}\text{In}_{20}$ (atomic %) versus temperature. The alloy has been prepared
16 at 280°C then solidified and introduced under air in the measurement cell.
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18 Figure 4: Resistivity of $\text{Bi}_{80}\text{In}_{20}$ (atomic %) versus temperature (expanded scale).
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20 Figure 5: Resistivity of sample 1 of $\text{Bi}_{20}\text{In}_{80}$ (atomic %) versus temperature. The alloy has
21 been prepared, outgased and heated at 1000°C then solidified and introduced under air in the
22 measurement cell.
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25 Figure 6: Resistivity of sample 2 of $\text{Bi}_{20}\text{In}_{80}$ (atomic %) versus temperature. The alloy has
26 been prepared, outgased and heated at 1000°C directly in the measurement cell then solidified
27 under argon, remelted and pushed into the capillary.
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30 Figure 7: Resistivity of sample 1 of $\text{In}_{75.54}\text{Pb}_{24.46}$ (atomic %) as function of temperature. Our
31 measurements compared to Yu et al. [2] obtained by digitalization.
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34 Figure 8: Resistivity of sample 2 of $\text{In}_{75.54}\text{Pb}_{24.46}$ (atomic %) versus temperature. Our
35 measurements compared to Yu et al. [2] obtained by digitalization.
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38 Figure 9: Resistivity of pure bismuth versus temperature. Our measurement compared to Xi et
39 al. [1] and to other authors.
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42 Figure 10: Resistivity of pure lead versus temperature. Our measurement compared to Yu et
43 al. [2] and to other authors.
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46 Figure 11: Resistivity of pure indium versus temperature. Our measurement compared to Xi et
47 al. [1] and to other authors.
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50 Figure 12: Resistivity of $\text{Bi}_{30}\text{In}_{70}$ (atomic %) as function of temperature. This experiment
51 shows that it is sometimes necessary to heat a long time (100 – 120H) at high temperatures
52 (1000°C) and to mix mechanically to obtain a homogenous alloy.
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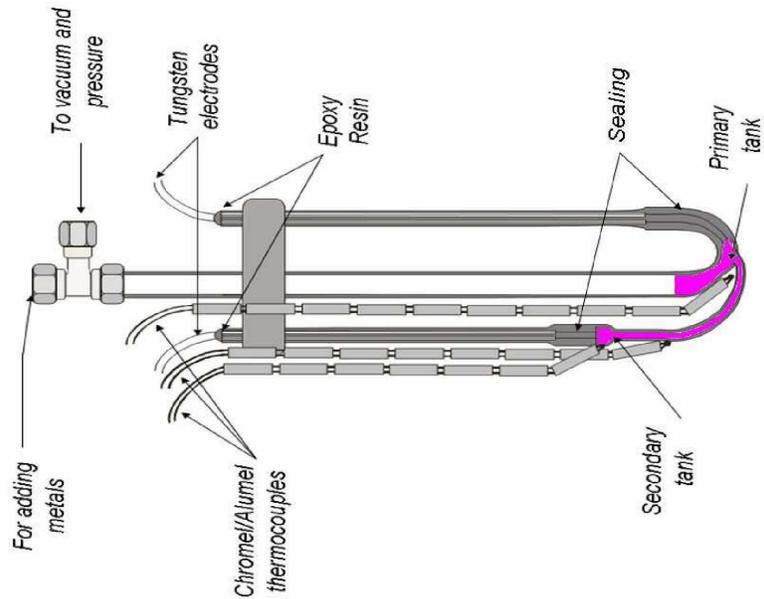


Figure 1: Quartz cell for resistivity measurements. The resistivity is measured by four tungsten electrodes. Temperature is measured outside using three K-type thermocouples. The concentration of the alloy can be changed by staying in the liquid state.
209x297mm (600 x 600 DPI)

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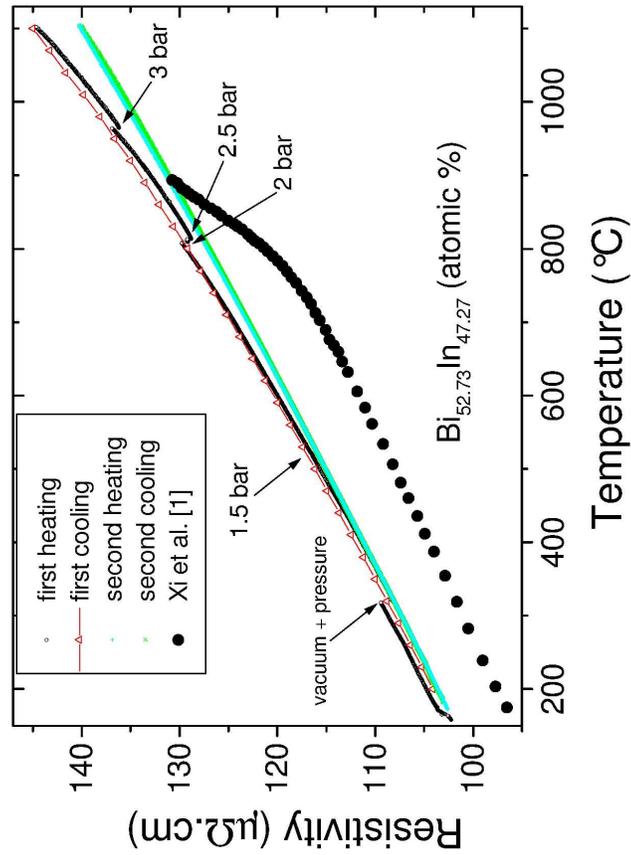


Figure 2: Resistivity of $\text{Bi}_{52.73}\text{In}_{47.27}$ (atomic %) as function of temperature. Our measurements compared to those of Xi et al. [1] obtained by digitalization.
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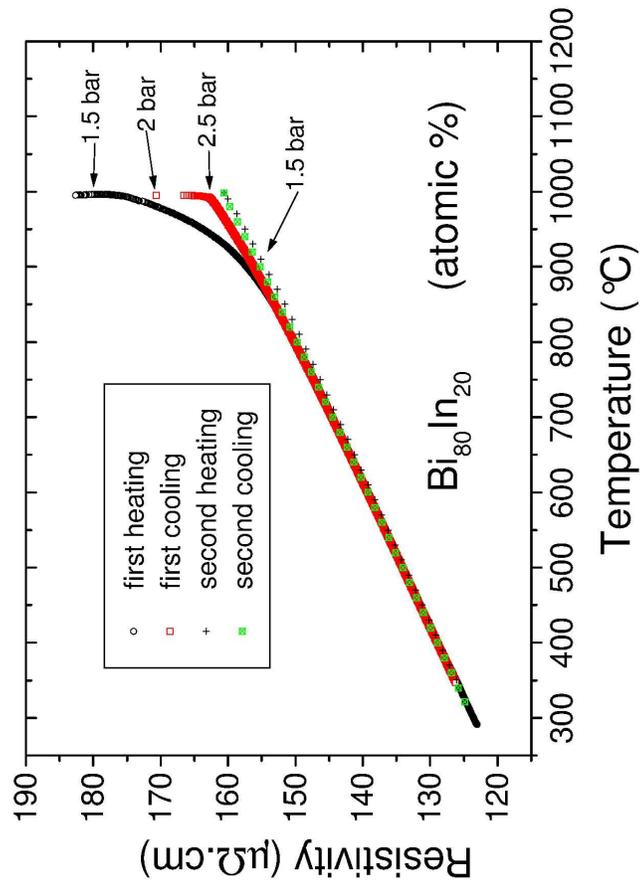


Figure 3: Resistivity of Bi₈₀In₂₀ (atomic %) versus temperature. The alloy has been prepared at 280°C then solidified and introduced under air in the measurement cell.
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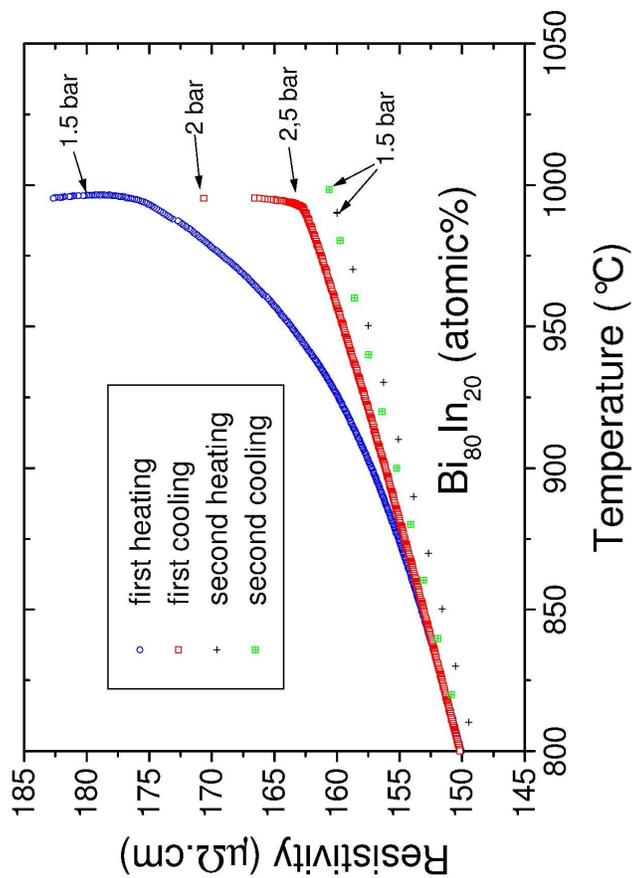


Figure 4: Resistivity of Bi80In20 (atomic %) versus temperature (expanded scale).
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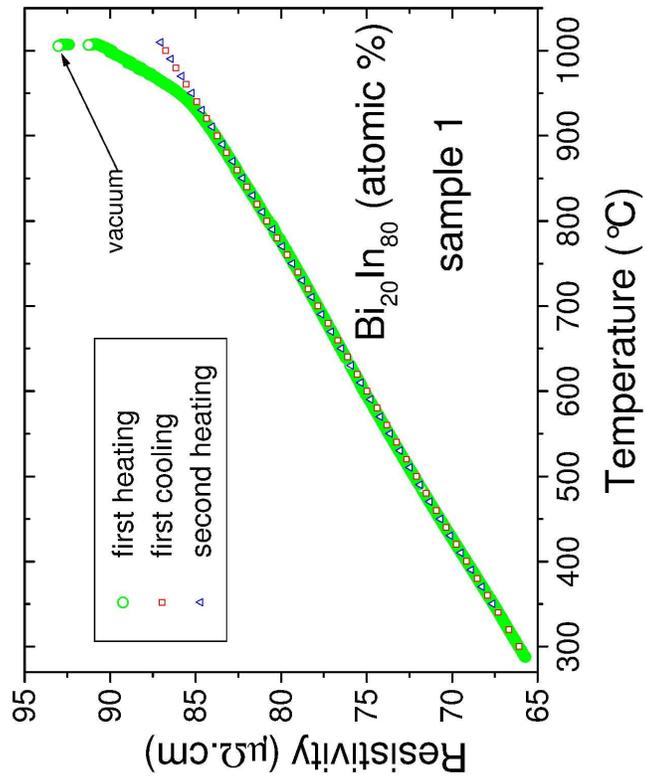


Figure 5: Resistivity of sample 1 of $\text{Bi}_{20}\text{In}_{80}$ (atomic %) versus temperature. The alloy has been prepared, outgassed and heated at 1000°C then solidified and introduced under air in the measurement cell.

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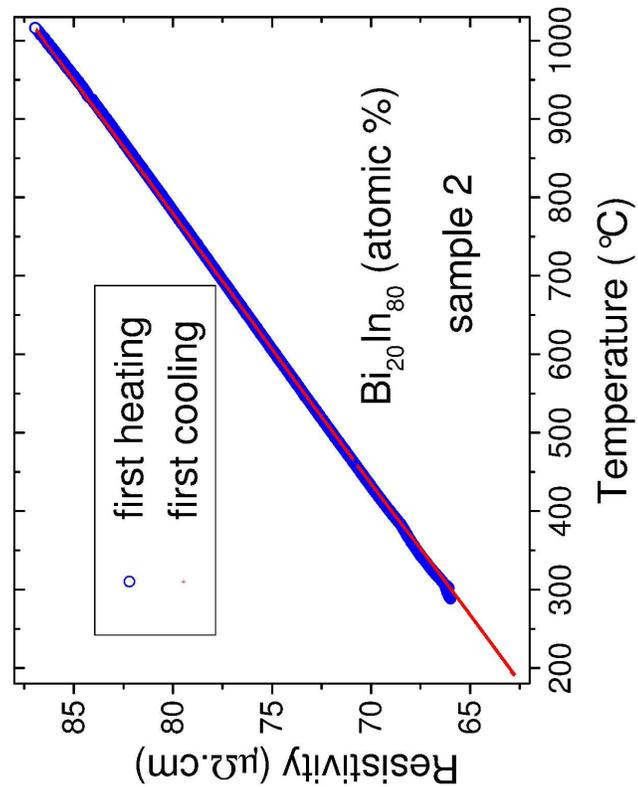


Figure 6: Resistivity of sample 2 of Bi₂₀In₈₀ (atomic %) versus temperature. The alloy has been prepared, outgased and heated at 1000°C directly in the measurement cell then solidified under argon, remelted and pushed into the capillary.

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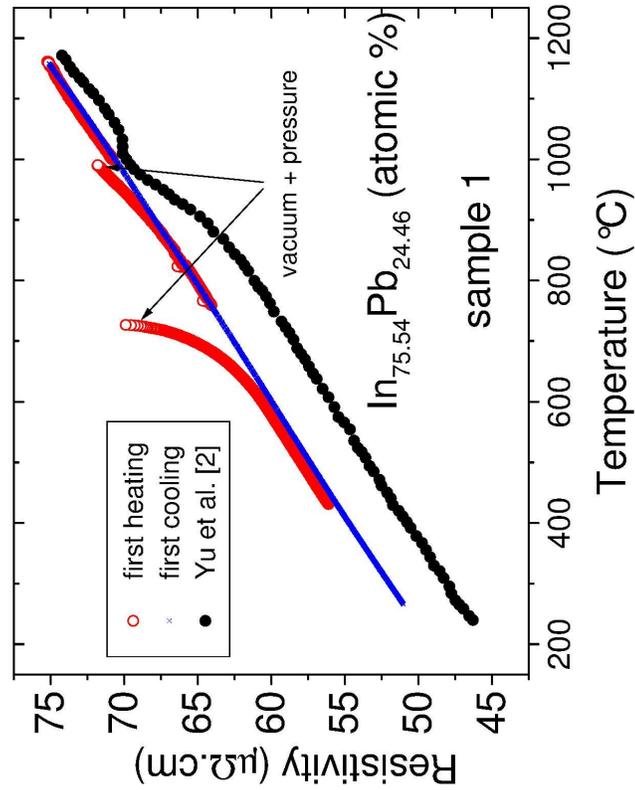


Figure 7: Resistivity of sample 1 of $\text{In}_{75.54}\text{Pb}_{24.46}$ (atomic %) as function of temperature. Our measurements compared to Yu et al. [2] obtained by digitalization.
209x297mm (600 x 600 DPI)

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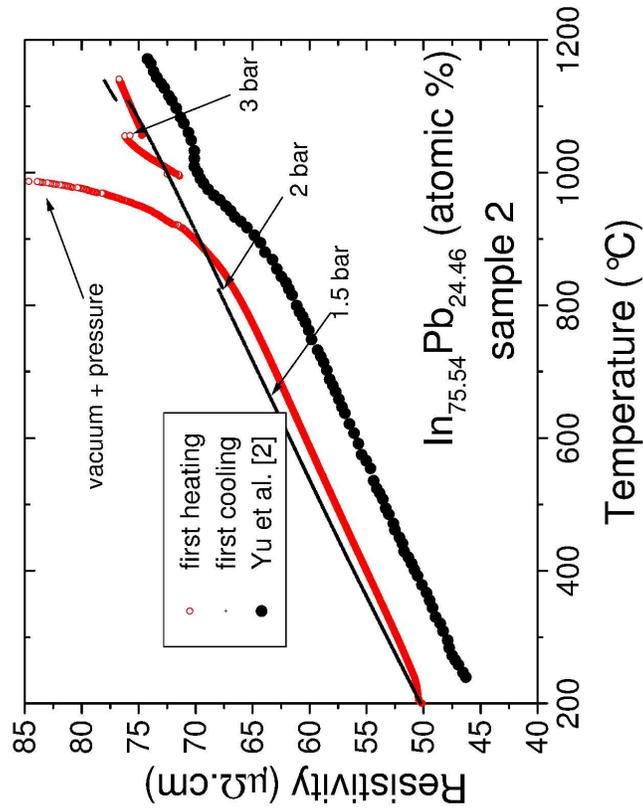


Figure 8: Resistivity of sample 2 of In_{75.54}Pb_{24.46} (atomic %) versus temperature. Our measurements compared to Yu et al. [2] obtained by digitalization.
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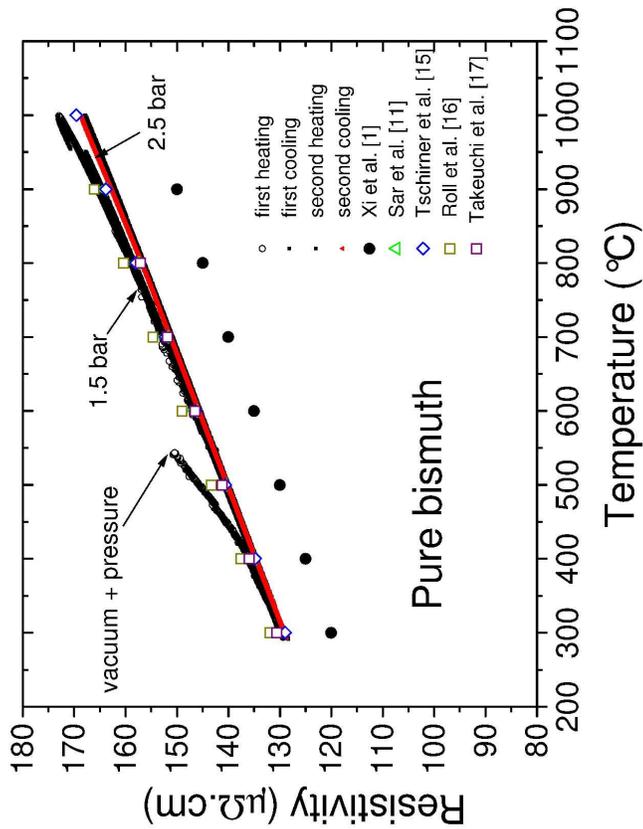


Figure 9: Resistivity of pure bismuth versus temperature. Our measurement compared to Xi et al. [1] and to other authors.
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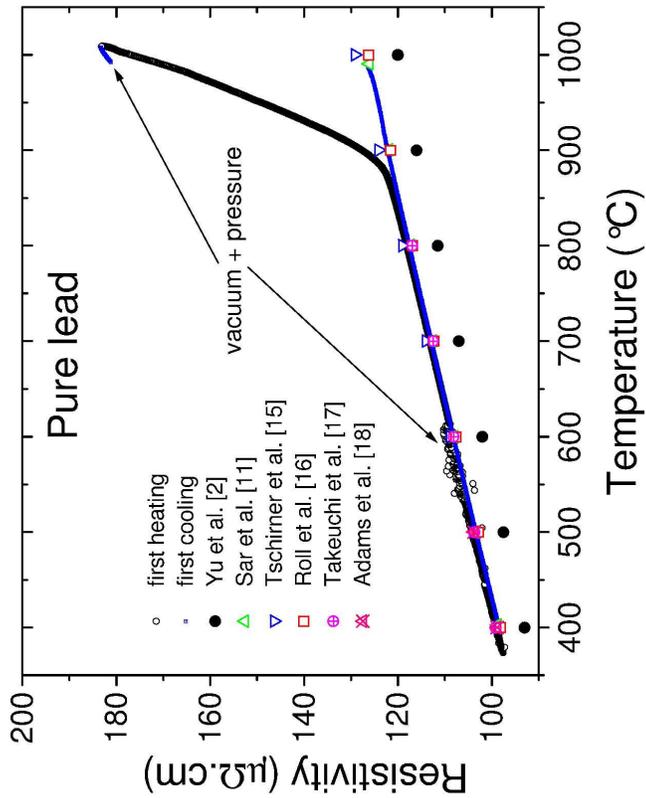


Figure 10: Resistivity of pure lead versus temperature. Our measurement compared to Yu et al. [2] and to other authors.
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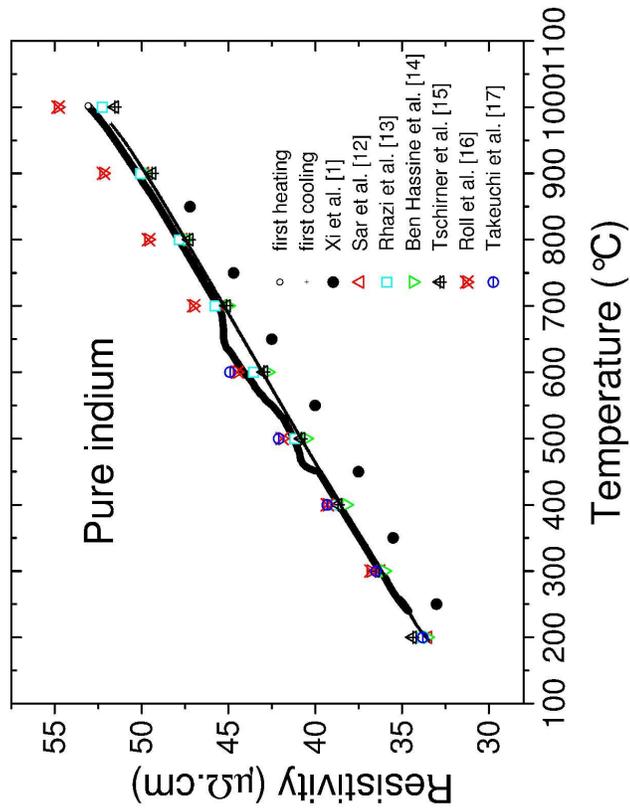


Figure 11: Resistivity of pure indium versus temperature. Our measurement compared to Xi et al. [1] and to other authors.
209x297mm (600 x 600 DPI)

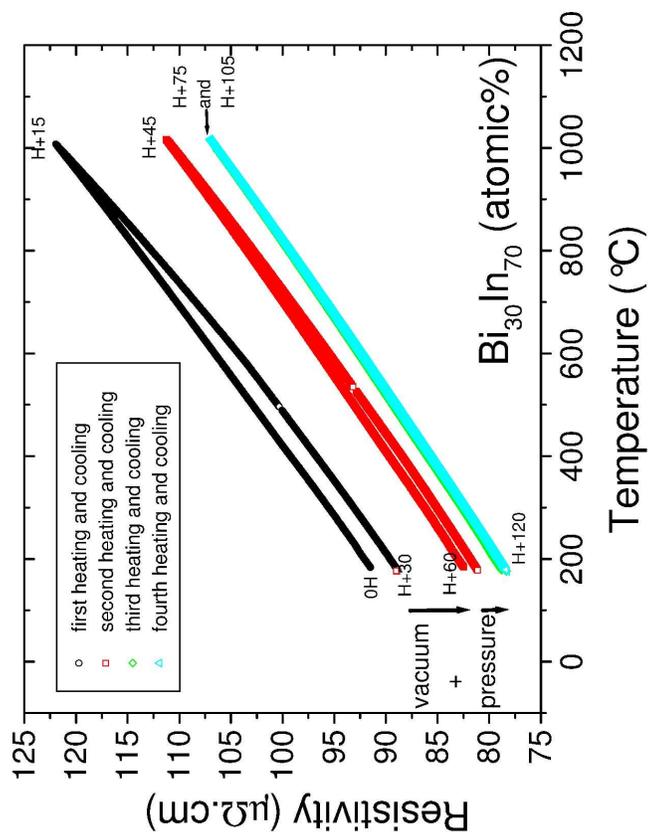


Figure 12: Resistivity of Bi₃₀In₇₀ (atomic %) as function of temperature. This experiment shows that it is sometimes necessary to heat a long time (100 – 120H) at high temperatures (1000°C) and to mix mechanically to obtain a homogenous alloy.

209x297mm (600 x 600 DPI)