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Electrical and thermal conductivity of soft solder at low temperatures

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Abstract. The electrical resistivity of soft solder ($Pb_{0\cdot 28}Sn_{0\cdot 72}$) has been measured in the temperature range 4·2 K to 300 K. The 'alloy' becomes electrically superconducting at a temperature of 6.9 K. Above this, in the entire temperature range, the resistivity could be described, apart from the residual resistivity, by the weighted average of the resistivities of the individual constituents which are derived from the Bloch-Grüneisen relation. The results are in accordance with the phase diagram, which shows a co-existence of two phases in almost the entire range of concentration of the Pb-Sn binary system. It has been shown that the thermal conductivity data on soft solder as well as on $Pb_{0\cdot 7}Sn_{0\cdot 3}$, both taken from literature, could be interpreted on the same basis, below and above the 'superconducting transition temperature'. Recent results on other Pb-Sn systems are discussed in the light of this interpretation.

Keywords. Resistivity; thermal conductivity; soft solder; Pb-Sn system; superconductivity; low temperature; phase-diagram.

1. Introduction

Soft solder is the eutectic composition of the Pb-Sn binary system used in electrical engineering. Its superconducting transition temperature (T_c) was required in connection with another study, and previous experimental measurements were not available. A preliminary measurement showed a T_c of 6·9 K, but the thermal conductivity measurement (Berman *et al* 1955) did not show any evidence of a transition around this temperature. In contrast, the thermal conductivity measurement (Mendelssohn and Olsen 1950) on another alloy $Pb_{0\cdot 7}$ $Sn_{0\cdot 3}$ exhibited a change in slope at 7 K which has been attributed to a superconducting transition occurring at that temperature. Also, the measured residual resistivity ratio (RRR) between room temperature and 7 K for soft solder was about 50, which is unusually high for a binary alloy.

This paper presents the results of the electrical resistivity measurements on soft solder in the temperature range 4·2 K–300 K. A calculation of the resistivity of Pb-Sn alloys is made on the Bloch-Grüneisen theory, consistent with the metallurgical phase diagram and compared with the experimental results. The thermal conductivity measurements on soft solder (Berman *et al* 1955) and on $Pb_{0\cdot 7}$ $Sn_{0\cdot 3}$ (Mendelssohn and Olsen 1950) are explained. The recent investigation (Chuah *et al* 1978) of the electrical and thermal conductivity of Pb-Sn alloys is discussed.

2. Experimental

Commercial soft solder with the composition of $Pb_{0.28}Sn_{0.72}$, corresponding to 60% Sn by weight was melted in a soldering iron to remove the resin flux and formed into a globule. The composition was checked by a chemical analysis. It was then pressed flat and cold-rolled into a thin sheet about 0·06 mm thick. A rectangular piece of 10 mm $\times$ 3 mm was mounted in a dipstick type vapour cryostat operated in conjunction with a temperature controller (Chandrasekaran *et al* 1979). The electrical resistance was measured by the d.c. four-probe method, in the temperature range 4·2 K to 300 K. A pair of 44 SWG copper wires (81 μ dia) enamel removed and coated with low thermal emf Cd-Sn solder, were directly pressed on to the sample and served as potential leads. These were joined to two other thicker copper leads, also with Cd-Sn solder and taken directly to the Keithley Model 148 nanovoltmeter without any further joints. With this arrangement, stray thermal emf in the circuit was restricted to less than 50 nV which was about two orders of magnitude smaller than the smallest signal measured. A current of 2 mA was passed in the sample.

Below 30 K, the temperatures were measured by a germanium resistance thermometer (GRT). This was previously calibrated by us using another GRT which was obtained from M/s. Cryocal, USA. In the region above 50 K, a platinum resistance thermometer was used. The temperature stability was better than ± 5 mK below 20 K and $\pm$ 0·25 K above 50 K.

3. Results

The electrical resistivity of soft solder is plotted against the temperature in figure 1. The form factor was determined by matching the measured resistance at room tem-

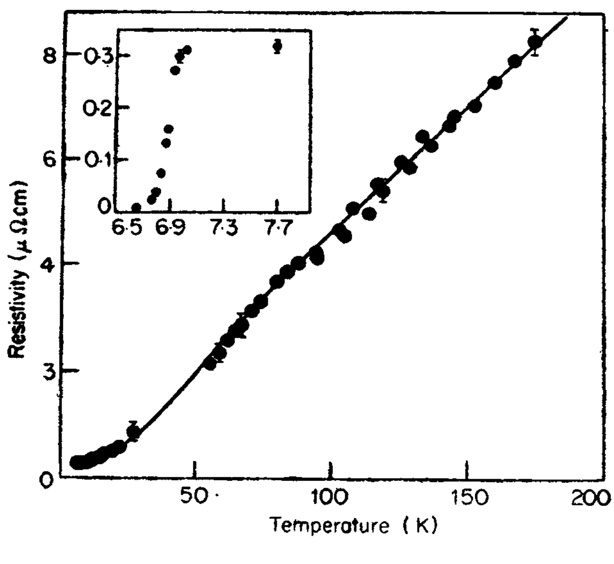

Figure 1. Electrical resistivity of soft solder as a function of temperature. The solid line is calculated using equations (1) and (2). The points represent experimental measurement. The inset shows the superconducting behaviour obtained in the resistivity measurement.

perature with the value of 15 $\mu\Omega$ cm (Harper 1972). The electrical resistivity is seen to decrease with temperature until about 8 K, when it becomes constant, at $0\cdot32\mu\Omega$ cm which is the residual resistivity. Then it falls sharply to zero, showing superconducting behaviour. The T_c, corresponding to the resistance drop of 50% of the normal state value, is 6·88 K. The width of the transition, defined as the interval in which the resistance changes from 10% to 90% is 70 mK.

4. Discussion

4.1. *Electrical resistivity*

The phase diagram of the Pb-Sn binary system is given in figure 2 (Hansen 1958). It is seen that at room temperature the solubility of Pb in Sn is negligibly small while that of Sn in Pb is only 3·2 atomic per cent. Thus almost throughout the composition range, the system exists in two phases, one phase with nearly 100% Sn while the other having 3.2 at. percent Sn in Pb. In the discussions that follow, we will approximate them to contain 100% Sn and 100% Pb respectively. Where necessary, specific remarks will be made regarding the presence of Sn in the Pb phase. It will also be assumed that the solubility of Sn in the Pb phase remains constant below room temperature. Though as yet, there is no direct evidence for this assumption, the results discussed in § 4.3 may imply that the solubility is finite. Optical micrograph pictures taken on the sample have indeed confirmed the co-existence of the two phases. If we assume that the crystallites of the two phases occur randomly in the alloy, which is again confirmed by optical micrographs in the case of soft solder, then the resistivity of the alloy could be represented by the equation

$$\rho^{\text{Pb-Sn}}(T) = \rho_0 + c\,\rho^{\text{Pb}}(T) + (1-c)\,\rho^{\text{Sn}}(T), \tag{1}$$

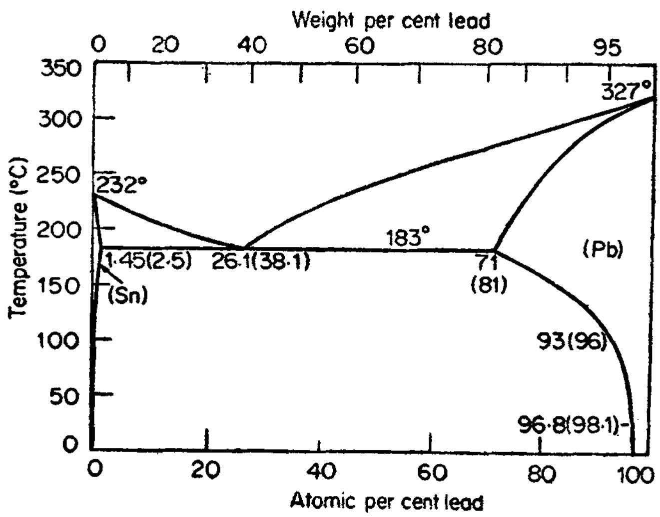

Figure 2. Phase diagram of Pb-Sn binary system (Hansen 1958). The room temperature solubility of Sn in Pb is shown. Figures in brackets represent weight percentages.

where ρ_0 is the residual resistivity of the alloy and c is the concentration of Pb. The residual resistivities of the Pb and Sn phases could be absorbed in ρ_0 and ρ^{Pb} and ρ^{Sn} regarded as ideal resistivities given by the Bloch-Grüneisen function

$$\rho(T) = 4A\,(T/\theta)^5\, I_5\,(\theta/T), \tag{2}$$

where A is a constant describing the electron-lattice interaction and θ the Debye temperature. The integral has the general definition

$$I_n\,(\theta/T) = \int_0^{\theta/T} \frac{z^n}{(e^z-1)\,(1-e^{-z})}\,dz. \tag{3}$$

In the high temperature limit, when $T \gg \theta$, (3) reduces to

$$I_n = [1/(n-1)]\;(\theta/T)^{n-1} \tag{4}$$

Using (4) in (2), and with the other input parameters shown in table 1, the constant A can be determined. The integral I_5 has been tabulated (McDonald 1956) as a function of T/θ. $\rho^{\mathrm{Pb}}(T)$ and $\rho^{\mathrm{Sn}}(T)$ can now be readily calculated from (2) and with the measured value of the residual resistivity ρ_0, used in (1) to give $\rho(T)$ of the alloy. This calculation has been carried out for soft solder and the result is shown in figure 1. The calculated resistivity is in excellent agreement with the experimental measurement in the temperature range 7–300 K. Figure 1 is restricted to 200 K, but the curve continues beyond with the same slope as at 200 K, all the way agreeing with the measurement. Thus, the resistivity of soft solder is the weighted average of the resistivities of the two phases at all temperatures apart from the additional impurity contribution. This result is quite general and should hold for all other compositions of the Pb-Sn system.

4.2. *Thermal conductivity*

In view of the ability of the 'two phase model' to explain the electrical resistivity, it can be expected that a similar approach might explain the thermal conductivity of these alloys, as the relaxation time involved in the thermal transport is the same as

Table 1. The Debye temperature, electrical resistivity at 0°C and the thermal conductivity in the high temperature limit used in expression (2) and (9).

	Debye temperature θ K	Electrical resistivity at 0°C $\mu\Omega$ cm	Thermal conductivity (high temperature limit) $W\,\mathrm{cm}^{-1}\,K^{-1}$
Pb	90[a]	19·2[b]	0·34[c]
Sn	160[a]	10·1[b]	0·63[c]
$\mathrm{Pb}_{0\cdot28}\,\mathrm{Sn}_{0\cdot72}$		15[d]	0·52[e]

[a]White (1968); [b]Meaden (1965); [c]Dwight (1972); [d]Harper 1972; [e]Berman *et al* (1955).

for electrical conduction in metals. The thermal conductivity measurements (Berman *et al* 1955) on soft solder are available, although no attempt to explain them has been made so far. Following (1), we can write for the total thermal resistivity (reciprocal of the thermal conductivity K) of the alloy as

$$W_e^{\text{Pb-Sn}}(T) = \frac{1}{K_e^{\text{Pb-Sn}}(T)} = W_{e,\,\text{imp}} + c\,W_e^{\text{Pb}} + (1-c)\,W_e^{\text{Sn}}. \tag{5}$$

K_e signifies the electronic contribution to the thermal conductivity which is the dominant one as against the lattice contribution which is not considered here. The first term in (5) is due to the scattering of electrons by the impurities and the other terms arise due to the scattering by the thermal phonons in Pb and Sn respectively. Once again on Bloch's theory, considering only the ideal thermal resistivity and neglecting impurity effects,

$$W_e = \frac{4A}{L_n(T)}(T/\theta)^5 \left[\left\{ 1 + \frac{3}{2\pi^2}\,\frac{\zeta}{D}(\theta/T)^2 \right\} I_5 - \frac{1}{2\pi^2} I_7 \right], \tag{6}$$

where ζ/D is a numerical parameter given in the free electron theory by

$$\zeta/D = 2^{1/3}\,N^{2/3}. \tag{7}$$

N being the number of conduction electrons per atom and has a value 2 for Pb and Sn, both belonging to the IV b group in the periodic table, and L_n is the Lorenz constant having the value $2{\cdot}45\times 10^{-8}\ W\,\Omega\,K^{-2}$ for metals. A is the same constant occurring earlier.

In the low temperature limit, the integrals become independent of temperature and have limiting values (Wilson 1953). The first and the third term in (6) can be neglected as they are proportional to $(T/\theta)^5$ and are small in comparison with the second term. Hence (6) reduces to the familiar expression

$$W_e = \alpha T^2, \tag{8}$$

where $\alpha = 151{\cdot}2/K_\infty\,\theta^2,$ (9)

and K_∞ is the value of the thermal conductivity in the high temperature limit. As was done in § 4.1 for the electrical resistivity, the total thermal resistivity for soft solder may be calculated using (5). But now, one is hampered by the lack of knowledge of the first term, viz., the impurity thermal resistivity. This is related to the residual electrical resistivity by

$$W_{\text{imp}} = \rho_0/L_n T = \beta/T, \tag{10}$$

and the electrical resistivity measurement on the same sample is not available. This difficulty can be overcome by fitting the experimental data to an expression of the form

$$W_e^{\text{Pb-Sn}}(T) = \frac{\beta}{T} + \gamma T^2 \tag{11}$$

where $\gamma = c\,\alpha_{\text{Pb}} + (1-c)\,\alpha_{\text{Sn}}.$ (12)

The thermal conductivity for soft solder calculated at selected temperatures in the range 8-20 K using the coefficients β and γ obtained from such a fit, are marked in figure 3. The experimental curve is also shown. The agreement between the two is very good establishing the validity of (11). Not so good, however, is the agreement between the value of γ calculated from the theory using (9) and (12) and that obtained from the fit of (11) to the experimental data. The values are shown in table 2 for soft solder and for pure Pb and Sn and also for sodium, which is considered a good Bloch metal. In the case of sodium, the corresponding coefficient is α and the calculated and the experimental values are given from (9) and (8).

It is seen from table 2 that there is no agreement between the calculated and the experimental γ values for Pb and Sn and even for sodium. Thus it is not surprising that the values do not agree for soft solder. In all the cases, however, the experimental value is smaller implying a lower phonon scattering contribution to the thermal resistivity.

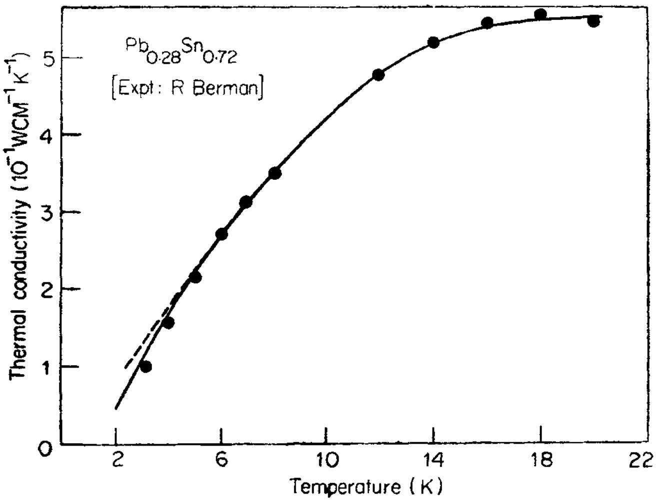

Figure 3. Thermal conductivity of soft solder as a function of temperature. The solid line represents the experimental measurement (Berman *et al* 1955). The points represent the fit of equation (11) to the experimental data above the temperature of 7 K and equation (15) below 7 K. The dashed line is the predicted thermal conductivity in the normal state obtained by the extrapolation of the impurity contribution to the thermal resistivity.

Table 2. The value of γ calculated by expression (12) and that obtained by a fit of expression (11) to the experimental data.

	Calculated	Experimental
Na	$1{\cdot}8 \times 10^{-3}$	$(3{\cdot}8 \times 10^{-4})^a$
Pb	$5{\cdot}5 \times 10^{-2}$	$(2{\cdot}9 \times 10^{-3})^b$
Sn	$9{\cdot}4 \times 10^{-3}$	$(6{\cdot}0 \times 10^{-4})^b$
$Pb_{0{\cdot}28}Sn_{0{\cdot}72}$	$2{\cdot}2 \times 10^{-2}$	$(1{\cdot}8 \times 10^{-3})^c$

[a]Berman and McDonald (1951); [b]Rosenberg (1955); [c]derived from the fit of expression (11) to the data of Berman *et al* (1955).

4.3. *Superconductivity*

Thermal conductivity measurements on $Pb_{0\cdot7}Sn_{0\cdot3}$ at low temperature have been carried out (Mendelssohn and Olsen 1950) both in the 'superconducting state' (with no magnetic field) and in the normal state (with an applied magnetic field) as depicted in figure 4. In the latter case, the thermal conductivity values are considerably higher as can be seen. From the change of slope with temperature in the former case, a superconducting transition has been suggested at 7 K. In a related work (Mendelssohn 1964) the remark has been made that the thermal conductivity in the two states could be described by the Heisenberg-Koppe relation

$$K_{es}/K_{en} = 2t^2/(1+t^4) = F(t), \tag{13}$$

where $t=T/T_c$, and K_{en} and K_{es}, the electronic contribution to the thermal conductivity in the normal and superconducting states. This claim is a little exaggerated and it turns out from what follows that a much better fit could be obtained to the experimental data by (13), if it is modified assuming that only the Pb-rich phase is superconducting while the Sn-rich phase is normal in the temperature interval $3{\cdot}7\,K<T<7\,K$, the lower limit being the transition temperature for Sn. Under this assumption, the T_c of 6·88 K obtained in the electrical conductivity measurement could be readily explained as due to the presence of a Pb phase short in the sample providing a supercurrent path. The observed T_c is lower than that of pure Pb, which is 7·2 K. This may be because of the presence of Sn in the Pb phase and may imply that the solubility of Sn is finite down to this temperature. Investigations are under way with small concentrations of Sn in Pb which may shed light on this aspect.

For the discussion of the thermal conductivity below T_c, (11) assumes a particularly simple form as at these low temperatures, $\gamma T^2 \ll \beta/T$ and can be neglected in com-

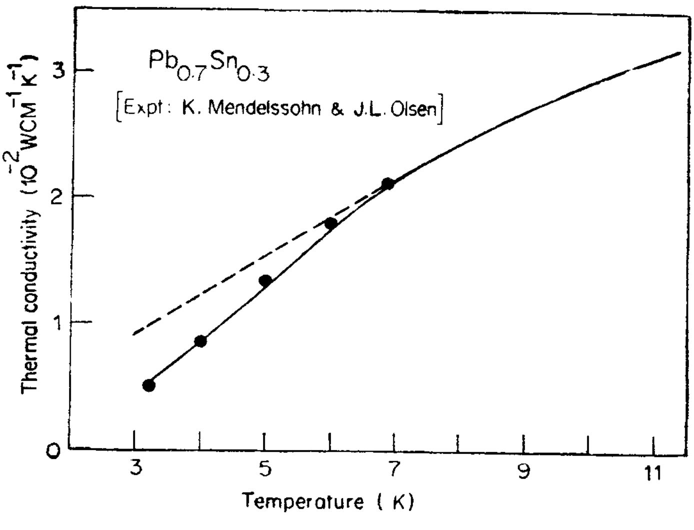

Figure 4. Thermal conductivity of $Pb_{0\cdot7}Sn_{0\cdot3}$ as a function of temperature. The solid line represents the experimental measurement (Mendelssohn and Olsen 1950) in the 'superconducting state' (with no magnetic field). The dashed line is the measurement by the same authors in the normal state (with an applied magnetic field). The points represent equation (15).

parison. This is to be expected since at low temperatures only the impurity scattering mechanism is dominant. Also the impurity contribution could be split up into two terms as arising due to Pb and Sn electrons separately. Since they have the same valence electron structure, these could be taken to be proportional to the concentrations. (11) can now be cast in the form

$$W_e = (\beta/T)\ [c + (1 - c)]. \tag{14}$$

Introducing this in (13), we get for $T > 3{\cdot}7$ K

$$W_{es} = (\beta/T)\ [cF(t) + (1 - c)]. \tag{15}$$

Thermal conductivity values calculated from (15) at selected temperatures are shown in figure 3 for soft solder and for $Pb_{0\cdot7}Sn_{0\cdot3}$ in figure 4. The experimental curves are also shown. In both the cases, the agreement between the experimental data and the calculated values is very good. Also plotted in the figures are the thermal conductivities in the completely normal states of the alloys. While for $Pb_{0\cdot7}Sn_{0\cdot3}$ this has been experimentally measured (Mendelssohn and Olsen 1950) by applying a magnetic field, the curve for soft solder is predicted from the calculated value of β.

Three remarks may now be made. First is that the thermal conductivity in the normal state is appreciably different from that in the ' superconducting state ' in the case of $Pb_{0\cdot7}Sn_{0\cdot3}$ while the difference is less perceivable for soft solder. This is not surprising as the superconducting phase is more predominant in the former alloy.

The residual electrical resistivity calculated from figure 4 by using (10) in the case of $Pb_{0\cdot7}Sn_{0\cdot3}$ is 8 $\mu\Omega$ cm which is very high compared to that measured for soft solder (in the present work) and also compared to that derived from the thermal conductivity data (Berman *et al* 1955). This has reflected in the much lower values for the thermal conductivity in the case of $Pb_{0\cdot7}Sn_{0\cdot3}$.

If the superconducting transition is traced by the mutual inductance method, we believe that the transitions of the individual phases may be obtained.

4.4. *Recent results in Pb-Sn system*

Electrical resistivity and the thermal conductivity measurements have recently been carried out (Chuah *et al* 1978) on Pb_xSn_{1-x} alloys (x=0·15, 0·3, 0·5 and 0·7 by weight) in the temperature range 7–300 K. In the case of the three alloys with x=0·3, 0·5 and 0·7, the measured resistivities could be well described by (1) within the experimental error quoted by the authors. In the case of the 0·15 alloy, the experimental curve was below that given by (1), just beyond the experimental error. In this alloy, the concentration of Pb is small (corresponds to 9 at. %) and the possibility exists of the presence of several Sn phase shorts in the sample. In such an event, the resistivity behaviour will be closer to that of Sn and will deviate from that obtained using (1) in conformity with the measurement.

However, the thermal conductivity measurements in these alloys could not be described by (5). In some of these alloys, the measured thermal conductivity is higher than the limiting value imposed by the impurity thermal resistivity. This investigation has been discussed in detail elsewhere (Radhakrishnan *et al* 1979).

5. Conclusions

The temperature variation of the thermal and electrical resistivities of the Pb-Sn alloys are given by the weighted average of the corresponding values in the individual phases apart from an additional impurity contribution. This result is quite general and should be applicable to other systems like Cd-Sn with similar phase diagram. This picture is also consistent with the superconducting behaviour of the alloys.

It is significant that although the sample used in our study is of commercial quality, the resistivity behaviour is in excellent agreement with the theory. This fact coupled with the large variation in resistivity between the room temperature and 7 K suggests the use of this alloy in low temperature applications for temperature measurement and control. The calibration is obtained by measurement of a single quantity, viz. the residual resistivity. Reducing this contribution in the alloy preparation, if possible, will help achieve higher thermal conductivity values which may be advantageous. But many systematic investigations are necessary before this suggestion can be taken too seriously.

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