Localized Phonons and Lattice Order Transformations in Thallium Based Alloys by Superconductive Tunneling*

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Abstract. Forced solutions of Tl plus 10 at. % of Na, Zn, Ag, Cd, or Sn and of Tl plus 6, 8, and 10 at. % In have been produced by vapour quenching upon a substrate cooled to 0.3 K. The lattice order of these, and similar pure Tl films, could be increased by annealing. The degree of order was mapped by changes in resistivity and in the phonon spectrum as studied by electron tunneling. As for lead based alloys, the stability of metastable disordered phases seems to be governed by the impurity melting temperature. Structure in superconductive tunneling curves, caused by localized phonon modes, was seen for In but not for the other impurities.

Introduction

We have studied (i) the occurrence of localized modes in the phonon spectrum of thallium based alloys, and (ii) changes in the structural order of a quench condensed alloy film upon annealing. The investigation is performed by electron tunneling complemented by resistivity versus temperature measurements.

Localized Phonons. When light impurity atoms are added to a heavy host matrix, peaks in the phonon spectrum may appear beyond the high frequency cutoff of the host. For low impurity concentrations, these additional, high frequency vibrational modes are localized in space. First discussed by Lifshitz [1], they have recently been investigated theoretically by numerical [2, 3] and analytical [4, 5] methods. Experimental evidence for their existence has been supplied by neutron scattering and superconductive tunneling. The Appendix contains a compilation of previous results.

Before this study, localized modes had been seen only in PbIn by the tunneling method (originally by Rowell et al.; Ref. 6) although several other lead based alloys had been investigated [7]. The absence of such modes in PbSn was particularly intriguing. In order to observe local modes by the tunneling method, several criteria must be fulfilled:

(i) The host must be a strong or medium coupling superconductor [8], i.e. neglecting transition metals only alloys based upon Pb, Hg, In, Tl, and Sn.

(ii) The atomic mass ratio \(M_{\text{imp}}/M_{\text{host}}\) must be sufficiently small—not very much bigger than 0.5 (for PbIn it is 0.56, cf. Appendix).

(iii) There must be a sufficiently large solid solubility. This limit could, in principle, be extended by making forced solutions, but

(iv) The film must have a long range lattice order [9].

The solid solubilities at room temperature and the mass ratios for the thallium based alloys used here are given in Table 1. Judging from the criteria (ii) and (iii) above, there appears to be a good chance to observe localized modes with In and Na (and possibly Zn) impurities—in the former case it was, indeed, possible to detect additional modes (a very brief account was given in Ref. 12). The lattice order requirement in (iv) must also be checked to test the possible appearance of local modes in any of the other alloys.

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Structural Order. A previous investigation of lead based alloys [13, 14] showed that the information of the phonon spectrum contained in superconductive tunneling curves could be used to classify the degree of lattice order. An amorphous state could be obtained by vapour quenching if the solubility of the components was very restricted. Transformations between successively more ordered states could be registered by changes in resistance during annealing. These transformations occurred within limited temperature regions, and the transformation temperatures could be correlated with the impurity melting points. This investigation, although less ambitious than the previous one, supports our earlier results.

Experimental Technique

Most of the experimental aspects are described in Refs. 14 and 15. Here we summarize the procedure and emphasize the details of particular interest to this work.

Appropriate amounts of the metals (purities and suppliers are given in Table 1) were sealed off under a reduced helium atmosphere in quartz tubes and melted in an RF-furnace. The melts were quenched in water. Wires were drawn, and small pieces of these were placed in the flash evaporation feeding mechanism. Tunnel junctions were fabricated by condensing cross strips upon an oxidized aluminium counter electrode situated on a single crystal quartz substrate cooled to 0.3 K. Pure Tl was evaporated from either Mo or W boats; alloys were evaporated by dropping small pieces onto a Mo boat and vapourizing independently. The build up of the film was monitored by a quartz crystal oscillator micro-balance. A single flash increased, on average, the film thickness by 1 nm. Although the vapour pressures of the different elements differ considerably at the source temperature, the compositional inhomogeneity is expected to be small due to the small amount evaporated in each flash. Final film thicknesses of about 50 nm were obtained.

Typical junction resistances were 5 to 100 Ω. The junctions were of good quality, and at zero bias their resistances in the superconducting state were at least two orders of magnitude larger than in the normal state.

Tunnel current (I) vs. voltage (V), dI/dV vs. V, and d2V/dI2 vs. V measurements were made in a bridge circuit similar to the one in Ref. 16. The second derivative data were registered on paper tape in an automatic data collection system [14]. The long integration time of this procedure allowed a detailed study of the phonon induced structure in the intermediate coupling superconductor Tl. The a.c. measuring signal was normally 200 μV RMS.

After measurements upon the films as deposited, these were slowly heated to final temperatures between 300 and 330 K. The film resistances were registered continuously and the heating was halted several times to check that the resistances represented thermal equilibrium values. Finally, the films were cooled again to 0.3 K, and new tunneling data were taken. An example of the changes in dI/dV for a Tl film is given in Fig. 1.

Superconducting transition temperatures, Tc, were measured with a commercially calibrated Ge resistor (Radiation Research CG-1 AC).

Table 1. Atomic mass ratios, solid solubilities in thallium and purities of metals used in this investigation

<table>
<thead>
<tr>
<th>Impurity element</th>
<th>M_{imp}/M_{Tl}</th>
<th>Solid solubility in Tl at. %</th>
<th>Metals used</th>
<th>Manufacturer purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.112</td>
<td>12</td>
<td>10</td>
<td>M.R. 4N</td>
</tr>
<tr>
<td>Zn</td>
<td>0.320</td>
<td>4</td>
<td>10</td>
<td>M.R. 5N</td>
</tr>
<tr>
<td>Ag</td>
<td>0.528</td>
<td>0</td>
<td>10</td>
<td>Eng. 5N</td>
</tr>
<tr>
<td>Cd</td>
<td>0.580</td>
<td>14</td>
<td>10</td>
<td>M.R. 5N5</td>
</tr>
<tr>
<td>In</td>
<td>0.562</td>
<td>14</td>
<td>10</td>
<td>M.R. 5N5</td>
</tr>
<tr>
<td>Sn</td>
<td>0.581</td>
<td>2</td>
<td>10</td>
<td>M.R. 5N</td>
</tr>
<tr>
<td>Tl</td>
<td></td>
<td></td>
<td></td>
<td>M.R. 5N</td>
</tr>
</tbody>
</table>

M.R.: Metals Research, Ltd; Eng.: Engelhard Ind., Inc.

Fig. 1. dI/dV vs. V for an Al/I/Tl (65 nm) junction as quench-condensed and as annealed at room temperature. Note the displaced scale. The curves were taken at 0.3 K with an a.c. signal of 200 μV RMS. Notice that the peak amplitude and the energy gap decrease after the heat treatment and that a shoulder develops just above the main peak (arrow). A structure of this kind was also observed by Clark (Ref. 17) who ascribed it to gap anisotropy.