Thermotransport of Noble Metal Impurities in Lead

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(Z. Naturforsch. 27 a, 138—140 [1972]; received 26 September 1971)

Steady-state distributions of Au, Ag and Cu tracers in Pb wafers subjected to temperature gradients have been determined. The effective heats of transport were $+5.8 \pm 1.1$ for Ag, -0.5 ± 0.3 for Au, and of the order of $+35$ for Cu (all in kcal/mole, positive values denoting the impurity migrating to the cold side of the Pb wafer). No significant temperature dependence of the heats of transport could be detected. The results are difficult to reconcile with existing theories of the intrinsic and electronic contribution to the heat of transport.

Thermotransport measurements on pure Pb metal have been carried out by THERNQUIST and LODDING [1], who found that the heat of transport was rather small ($Q^*_{\text{Pb}} = +2.1 \pm 4.0$ kcal/mole). Noble metal impurities in Pb are known [2] to diffuse much faster than do the matrix atoms; it is therefore believed [2, 3] that these elements probably move interstitially in Pb. Final proof of this, however, has yet to be supplied. It is from this point of view and from that of elucidating the thermotransport mechanisms in metals, that the present study was undertaken. Interstitial impurities should classically [4] have a positive intrinsic heat of transport, i. e. with the solute moving to the cold end. If one neglects the effects of phonons and of electronic heat carriers, which present theories [5] predict to be fairly small for impurities in Pb, the heat of transport should approximately equal the activation energy of impurity diffusion. Very preliminary results by ANTHONY [6] indicated, however, that the value of Q^* for Au in Pb is essentially zero and for Ag in Pb positive but very small. Diffusion data for Cu, Au and Ag in Pb have been compiled by DYSON et al. [2], and the activation energies are, respectively, 8.02, 9.35 and 14.44 kcal/mole. The purpose of this investigations has been to obtain the corresponding heats of transport. For Au and Ag it was hoped to reach a better accuracy then Ref. [6], while at least semi-quantitative data were aimed at for hitherto unstudied Cu in Pb.

Single crystal cylinders of Pb, 1.3 cm in diameter, were grown by the Bridgman method under vacuum from 5 N purity material. They were cut into wafers, 0.6 to 3.6 mm thick, by a spark cutter. For the Au and Ag experiments radioactive tracers (^{195}Au and $^{110\text{m}}$Ag) were used; each wafer was sectioned by microtome after the anneal, and the slices were weighed and counted. For the Cu experiments, natural Cu from a $\text{CuCl} - \text{HNO}_3$ solution was used and the profile was determined by a Cameca secondary ion microprobe analyzer, sputtering along a section perpendicular to the cylinder face. In all cases, the impurity was applied in HNO_3 solution to one surface of the lead wafer, which had been etched to shiny lustre by a solution of 3/4 acetic acid and 1/4 concentrated H_2O_2. The wafers were then annealed under vacuum, usually at a temperature slightly below that intended for the investigation (to reduce the likelihood of precipitation) and for a sufficient number of days to diffusion saturate the specimen. All traces of impurity left on the surface were then removed by dissolving off several hundred microns of the Pb surface in a $\text{CH}_3\text{COOH} - \text{H}_2\text{O}_2$ solution.

The sample was placed in an evacuated (about 10^{-6} Torr) chamber between two Cu blocks, with intervening Mo sheets to prevent contamination. The top block was heated electrically and the bottom block was "cooled" by a hot oil bath. Temperatures were controlled to about ±1 °C. The temperature gradient, usually about 100 °C/cm, was calculated from the heat flow in a cylinder of pure Cu in series with the Pb wafer. The flow was measured by two calibrated thermocouples a carefully measured distance apart, and found to be in essential agrement with the power input to the heater. The temperature of the Pb specimen itself was usually measured by a separate thermocouple embedded into the side of the wafer or, for very thin samples, was estimated within ±10 °C from the temperatures in the Cu blocks above and below the sample.

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The sectioning and counting procedure employed here for Au and Ag in Pb has been described elsewhere[7]. For the stable Cu tracer profile in Pb an IMS 300 ion microanalyzer (Cameca) was used. As the diffusion coefficient of Cu in Pb at room temperature is of the order of 10^{-6} cm^2/sec, back-diffusion had to be suppressed by keeping the samples in liquid nitrogen between anneal and analysis. For microanalyzer study, the wafer was cut parallel to the cylinder axis. In the ion source sample holder, the sputtering O_2^- beam was focused on the freshly cut surface. The holder has then moved to and fro (about 0.5 mm/min) in a sense perpendicular to the butt face of the wafer. This was repeated along several scanning lines across the cut surface. The sputtered Cu-ion yield was recorded as function of position on the scanning line, and found to increase rather smoothly by about a factor 4 from the "hot" to the "cold" face of the Pb wafer.

The effective heat of transport, Q^*, was calculated from the steady-state balance between drift and back-diffusion,

$$(c_i D_i Q^*/R T^2)\, dT/dx = (dc_i/dx)\, D_i\,,$$

or

$$d \ln c_i / d(1/T) = Q^*/R\,.$$

In the analysis of Q^* correlation and defect flow effects have been neglected on the assumption that the impurity moves interstitially. Furthermore, the self-transport motion of Pb atoms can be neglected since the self-diffusion coefficient is at least three orders of magnitude smaller than that of the noble metal impurities[2, 8].

Figures 1 through 3 show representative results for the impurities Au, Ag and Cu. Table 1 lists the heats of transport and the mean specimen temperatures. The errors quoted for Au and Ag represent deviations from least squares fits and do not account for systematic errors, such as those in specimen temperature (not greater than ±5% in Q^* for samples without thermocouples) or in temperature gradient (at most a few percent). No statistically significant temperature dependence of Q^* could be

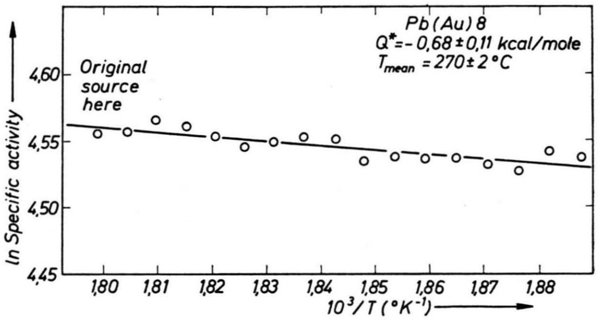

Fig. 1. Concentration profile of Au in Pb, steady-state thermotransport.

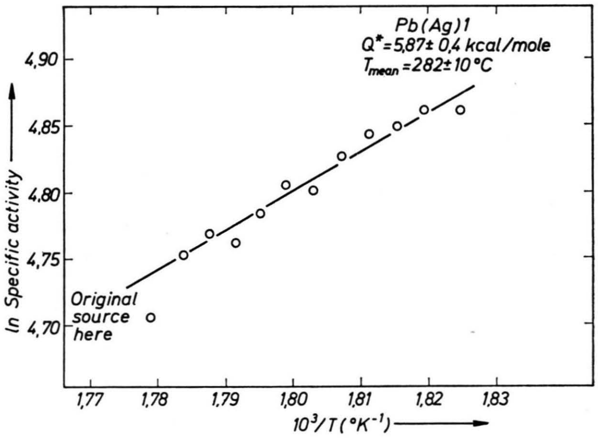

Fig. 2. Concentration profile of Ag in Pb, steady-state thermotransport.

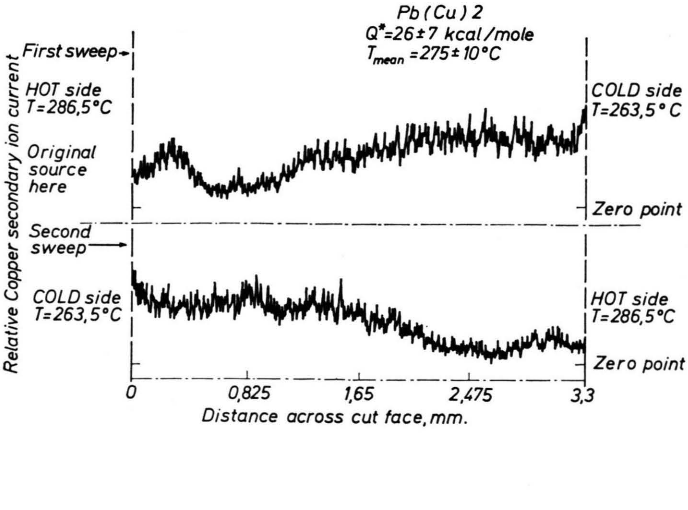

Fig. 3. Concentration profile of Cu in Pb, steady-state thermotransport.

Table 1. Effective heats of transport for Au, Ag and Cu impurities in Pb.

Specimen	Heat of Transport, Q^*	Average Temperature	Separate Thermocouple	Side of original source
Pb(Au) 4	-0.93 ± 0.38	254 ± 10 deg. C	No	Hot + Cold
Pb(Au) 7	-0.41 ± 0.40	271 ± 10	No	Hot
Pb(Au) 8	-0.68 ± 0.11	270 ± 2	Yes	Hot
Pb(Au) 9	-0.12 ± 0.12	293 ± 2	Yes	Cold
Pb(Au) 13	-0.35 ± 0.57	280 ± 2	Yes	Cold
Average, Au	-0.5 ± 0.3 kcal/mole			
Pb(Ag) 1	$+5.87 \pm 0.40$	282 ± 10	No	Hot
Pb(Ag) 2	$+6.96 \pm 0.61$	270 ± 2	Yes	Hot
Pb(Ag) 6	$+6.90 \pm 1.12$	221 ± 10	No	Hot
Pb(Ag) 7	$+4.80 \pm 0.31$	291 ± 2	Yes	Hot
Pg(Ag) 8	$+4.39 \pm 0.42$	290 ± 10	No	Hot
Pb(Ag) 9	$+5.79 \pm 1.35$	209 ± 10	No	Hot
Average, Ag	$+5.8 \pm 1.1$ kcal/mole			
Pb(Cu) 1	$+44 \pm 9$	277 ± 2	Yes	Hot
Pb(Cu) 2	$+26 \pm 7$	275 ± 10	No	Hot
Average, Cu	$+35 \pm 10$ kcal/mole			

detected. Attempts to measure Q^* for Au at a lower temperature (about 125 °C) failed, as the concentration profiles were extremely erratic, possibly due to Au precipitation at dislocations. The errors quoted for Cu are based on averaging several sweeps with the sputtering beam.

Table 1 shows that the heat of transport of Au in Pb is not only very small, but slightly negative within the r.m.s. errors. This is difficult to explain in terms of classical kinetics for interstitial thermotransport. According to the theoretical treatments given by Gerl and by Fiks [5] the electronic contribution should be less than about -0.05 kcal/mole, if an effective charge number of $Z^* = -0.75$ (the maximum allowed by the electrotransport work by Schwarz and Stöckert [9]) is assumed.

The Q^* value for Ag in Pb (Table 1) is positive and slightly less than half the activation energy of impurity diffusion, a result analogous to that for Au in Li, obtained by Thernquist [10]. A Z^* of -8 (210 °C) to $+2.75$ (300 °C) from the work of Kuz'menko et al. [11] would lead to an electronic contribution to Q^* which is still at most some ±4% of the diffusion activation energy.

For Cu in Pb the heat of transport (Table 1) is 3 to 5.5 times the diffusion energy; as the ion probe analysis is less proven by experience than radioactive tracer analysis, it is only safe to claim that Q^* for Cu in Pb is large and positive. The result is qualitatively similar to that for Cd in Li [10], and at any rate is difficult to reconcile with a straightforward interstitial mechanism.

The phonon contribution to the heat of transport is presently not readily calculable from existing models [5, 12], and may possibly contain the key to the interpretation of the present results.

This work was supported by the Swedish Board for Technical Development. We are indebted to Docent A. Lodding for encouragement and discussion, and to Ing. H. Olsson for technical assistance. We are particularly obliged to Cameca (Courbevoie, France) for allowing us to use an IMS 300 instrument at their plant.

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