The resistivity and thermoelectric power of liquid antimony

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ABSTRACT

The resistivity ρ, and thermoelectric power S of liquid antimony have been measured as a function of temperature. The experimental data are compared with theoretical predictions based on the use of the single-site t-matrix within a nearly-free-electron framework. These and other similar calculations show that both ρ and $d\rho/dT$ are strongly dependent on the initial choice of potential.

Liquid Sb (obtained from Koch Light Laboratories Ltd, with a designated purity of 99·999%) was contained in a fused silica tube and the resistivity measured using a four-probe d.c. method. Electrical contact with the liquid sample was made via a thin molybdenum foil (Howe and Enderby 1967) to which chromel and alumel leads were attached. The same probes were used to determine the absolute thermoelectric power of liquid Sb by measuring the temperature variation of the Seebeck voltage generated by a chromel–antimony–chromel couple. This use of chromel as a counter electrode necessitated a series of calibration experiments in which the thermoelectric power of chromel was measured using platinum and copper as reference electrodes (Cusack and Kendall 1958). Over a range of temperatures T, from 450 to 1250°C, it was established that the absolute thermoelectric power of chromel could be represented by the linear expression

$$S_{\mathrm{ch}} = 31 \cdot 41 - 0 \cdot 02233 T \quad (\mu V\ K^{-1})$$

to an accuracy greater than $\pm 0 \cdot 5\ \mu V\ K^{-1}$.

In a subsequent experiment, the measurement of the thermoelectric power of liquid Sb was repeated, using a copper counter electrode, with almost identical results. The results obtained for the resistivity ρ and thermoelectric power S of liquid Sb are presented in fig. 1 as a function of temperature where a comparison is made with other published values of the resistivity. In the table the experimentally determined values of the resistivity, thermoelectric power and their temperature derivatives are evaluated at the melting point (630°C) and compared with the calculated values.

The resistivity ρ was calculated using the general single-site scattering matrix formulation of the Faber–Ziman theory (Ziman 1967, Evans, Greenwood and Lloyd 1971). The final expression used for ρ has been simplified by making the usual assumption that the backscattering is dominant, but there is no

justification in this case for any further approximations of the type made possible when a single phase shift is dominant at the Fermi energy (such as η_2 in transition metals where d-type scattering dominates). Thus

$$\rho = (24\pi^3\hbar^3/me^2)[a(2k_F)|f(\pi)|^2]/\Omega_0 E_F \qquad (1)$$

Fig. 1
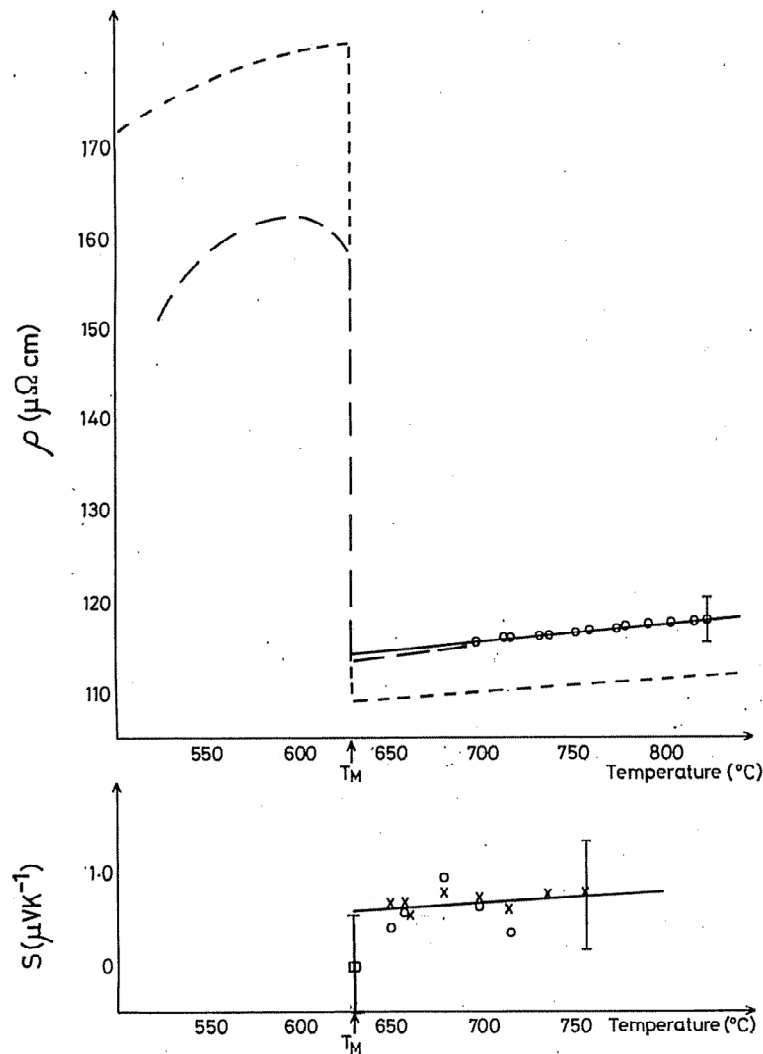
Antimony : resistivity (○, present work ; long-dashed line, Roll and Motz (1957) ; short-dashed line, Busch and Tieche (1963) ; solid line, Gasser and Kleim (1977)) and thermoelectric power (○, present work using chromel electrodes ; ×, present work using copper electrodes ; □, Enderby, van Zytveld, Howe and Mian (1968)).

Comparison between measured and calculated values of the resistivity, thermoelectric power and their temperature derivatives for pure Sb at 630°C.

	Resistivity, ρ ($\mu\Omega$ cm)	$\partial\rho/\partial T$ ($\mu\Omega$ cm K^{-1})	Thermopower, S (μV K^{-1})	$\partial S/\partial T$ (μV K^{-2})
Measured	114·2 ($\pm 1\cdot 5$)	0·02 ($\pm 0\cdot 01$)	0·58 ($\pm 0\cdot 60$)	0·001 ($\pm 0\cdot 001$)
Theory with $R_{\mathrm{TF}}=0\cdot 475$ Å	121	$-0\cdot 002$	$-1\cdot 0$	—
Theory with $R_{\mathrm{TF}}=0\cdot 550$ Å	291	0·006	1·0	—

where the backscattering factor, $f(\pi)$, is related to the single-site t-matrix, $t(k)$, via a summation over different phase shifts :

$$f(\pi) = 1/k \sum_{l=0}^{\infty} (2l+1) \sin \eta_l \exp (i\eta_l) P_l(\pi)$$

$$= -[\dot{m}(2mE)^{1/2}\Omega_0/2\pi\hbar^3 k]t(2k_{\mathrm{F}})$$

The thermoelectric power was then obtained from the resistivity by using the Boltzmann equation, which gives

$$S = -(\pi^2/3)(K_{\mathrm{B}}^2 \, T/e)(\partial \ln \rho/\partial E), \qquad (2)$$

where $\partial \ln \rho/\partial E$ is evaluated at the Fermi energy. $f(\pi)$ was calculated as a function of energy using a muffin-tin truncation of the Ashcroft empty-core pseudopotential (Cohen and Heine 1970) which contains two adjustable parameters : the core radius, R_c, and the screening length, R_{TF}. These were varied over a small range to determine the sensitivity of the resistivity to the scattering potential. A Hartree–Fock–Slater calculation, performed for just two values of the exchange parameter, α, produced similar results for $f(\pi)$. This suggests that the present calculations are reasonable and that there would be little to gain from undertaking a full Hartree–Fock–Slater treatment. The Fermi energy was obtained as a function of temperature by assuming a free-electron density of states and using the known temperature variation of the liquid density (Weast 1974). The structure factor, $a(K)$, was taken from the data of Waseda and Suzuki (1971) and when used in conjunction with the calculated, free-electron values of k_{F} produced the same value for $a(2k_{\mathrm{F}})$ at the two temperatures of 660 and 800°C. Accordingly, this value was adopted for the whole of the temperature range.

The core radius for antimony is fixed by band-structure calculations (Cohen and Heine 1970) at around 0·58 Å, and this value was used. The screening constant is not so well defined : at the $q=0$ limit of the pseudopotential it is given as 0·48 Å, but band-structure calculations (Bullett 1975) suggest a somewhat larger value. Calculations of ρ were made for R_{TF} in the range 0·4 to 0·6 Å (these correspond to values of V_{100} in the range 1·4–1·7 eV, and Bullett's calculation suggests 1·5 eV for this parameter). Within this range the backscattering factor varies by a factor of two (see fig. 2), giving resistivities

Fig. 2
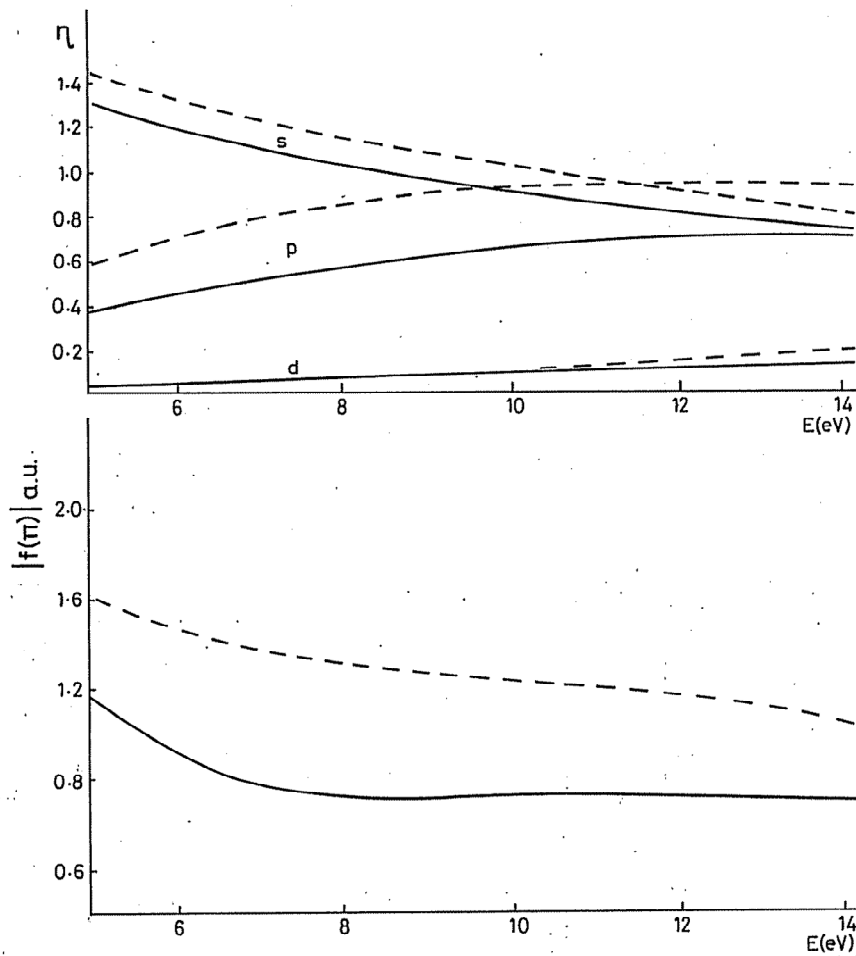
Antimony : phase shifts and backscattering factor ; $R_0 = 0.58$ Å, energies relative to muffin-tin level (solid line, $R_{TF} = 0.475$ Å ; dashed line, $R_{TF} = 0.550$ Å). The calculated free-electron value of E_F is 10·88 eV at 630°C.

that range from 80 to 360 $\mu\Omega$ cm. The best agreement with the experimentally determined value of ρ was obtained for $R_{TF} = 0.475$ Å. Furthermore, the backscattering factor as shown in fig. 2 is indicative of the weak scattering nature of this system, a point that is consistent with these calculations. The temperature coefficient $\partial\rho/\partial T$ and thermopower S were calculated subsequently from the resistivity. There is a tendency for these to assume negative values on account of the positive thermal expansion, but this is counterbalanced by the increase in $f(\pi)$ with decreasing energy so that both $\partial\rho/\partial T$ and S are positive for $R_{TF} > 0.53$ Å. Over the range of screening lengths used, $(1/\rho)(\partial\rho/\partial T)$ lay between $\pm 3 \times 10^{-5}$ K^{-1} and S between ± 1 μV K^{-1}, and the best fit to the data used $R_{TF} = 0.56$ Å. As shown in the table, it was found impossible to fit both

ρ and S simultaneously. Furthermore, the theory shows that both S and $\partial\rho/\partial T$ should become negative at temperature above $\sim 1000°C$, which is not in agreement with experiment (Gasser and Kleim 1977).

We conclude that the sensitivity of ρ to $f(\pi)$ makes calculations of ρ from a potential fixed by band-structure calculations of limited value. The assumption of the dominance of backscattering may lead to sufficient errors to cause S to have the wrong sign. The calculation could, in principle, be improved by using the full integral over all scattering directions, but the extreme sensitivity of ρ makes it unlikely that useful data could be obtained simply by incorporating potentials derived from other experiments.

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