Thermochimica Acta, 135 (1988) 179–185
Elsevier Science Publishers B.V., Amsterdam

MAY SCHOTTKY TYPE DEFECTS IN METALS BE STUDIED BY ANALYSING THEIR SPECIFIC HEAT DATA ?

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ABSTRACT

An attempt to determine vacancies formation parameters in metals, by carefully analysing the temperature dependence of the specific heat data (C_p vs T), is carried out. The values determined for the various parameters differ considerably from those determined by other techniques. This indicates that C_p vs T in metals, near their melting points, is not as sensitive to point defect formation as to other processes which play a role and of which the precise mechanism or origin is not at all clear. However, it is shown that its particular mathematical form is quite close to that of point defect formation processes.

INTRODUCTION

Point defects of the Schottky type (lattice vacancies) in metallic systems such as Al, Au, Ag and Cu have been detected and studied by a number of techniques (1), but not by that of the specific heat even though it is well known that point defects make a characteristic contribution (2). It is the aim of this work to carefully analyse the specific heat data from below liquid helium temperatures up to their melting points, and to learn about the possibility and ability of these analyses to determine the existence of vacancies and of their characteristic parameters.

THEORY

The four metallic elements to be analysed in this work are isomorphous crystals of a fcc structure, with one atom per primitive unit cell (3). Therefore, the normal modes are acoustic, and it will be assumed that their contribution to the specific heat as a function of temperature may be described by

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

Debye's model (3) with adequate corrections to account for anharmonic effects (4,5).

Taking into account the contributions due to vacancies formation (1,2), and to the conduction electrons (3), we may write:

$$C(T) = \gamma T + \frac{9\,R}{1-c_D T}\,\frac{T^3}{T_D^3}\int_0^{T_D/T}\frac{x^4\,e^x}{(e^x-1)^2}\,dx + R\exp(S_f/k)\left(\frac{E_f}{kT}\right)^2\exp(-E_f/kT) \qquad (1)$$

where the first term describes the conduction electron contribution to C_p vs T, while the second and the third terms describe the contributions due to acoustic modes and vacancies formation, respectively. The meaning of the various symbols is that given in standard texts (3); S_f and E_f are the entropy and the energy associated to vacancy formation. The Debye temperature T_D has been assumed to exhibit an average linear temperature dependence $T_D = T_{oD}\,(1 - c_D\,T)$.

At low temperatures (T < 5 K) Eq. 1 becomes:

$$C_p(T) = \gamma T + \frac{12\,R\,\pi^4}{5\,\Theta_D^3}T^3 \qquad (2)$$

where Θ_D is generally known as the Debye temperature at 0 K.

RESULTS

The C_p vs T data for Al, Ag, Au and Cu were collected from Refs. 6 and 7, and from the references there in mentioned. The data in the temperature range 0 < T < 300 K is abundant and quite similar data were found by the various authors. However, above 300 K and up to the corresponding melting points the amount of data is much more scarce and the similarity of data found by various authors greatly reduced, an extreme case being that of Au where the two sets of data reported in Refs. 1 and 7 produce quite different results as shown below and in the E_f values shown in Table I.

The fittings in all four cases were carried on as follows. All of them are non-linear least squares fits following the procedure developed by Deming (8). First, by fitting the C_p vs T

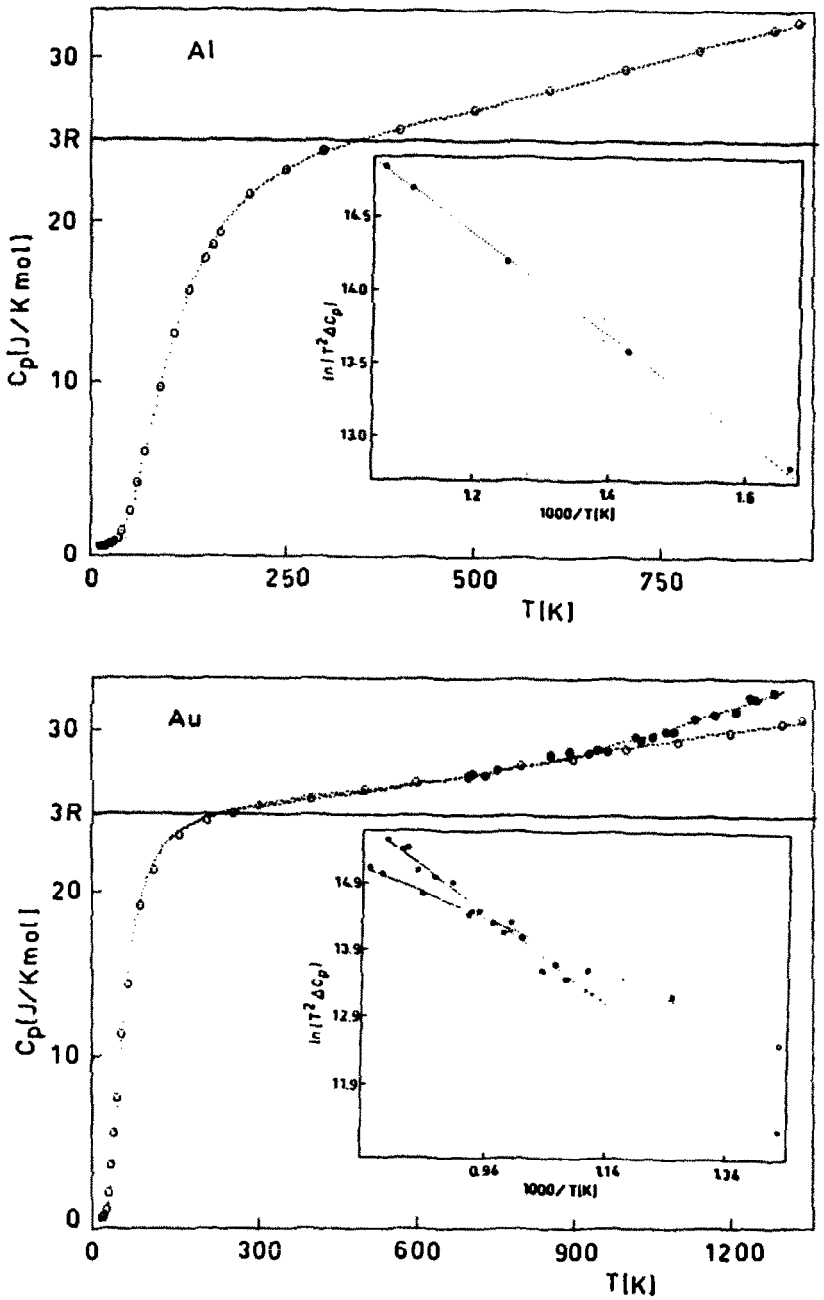
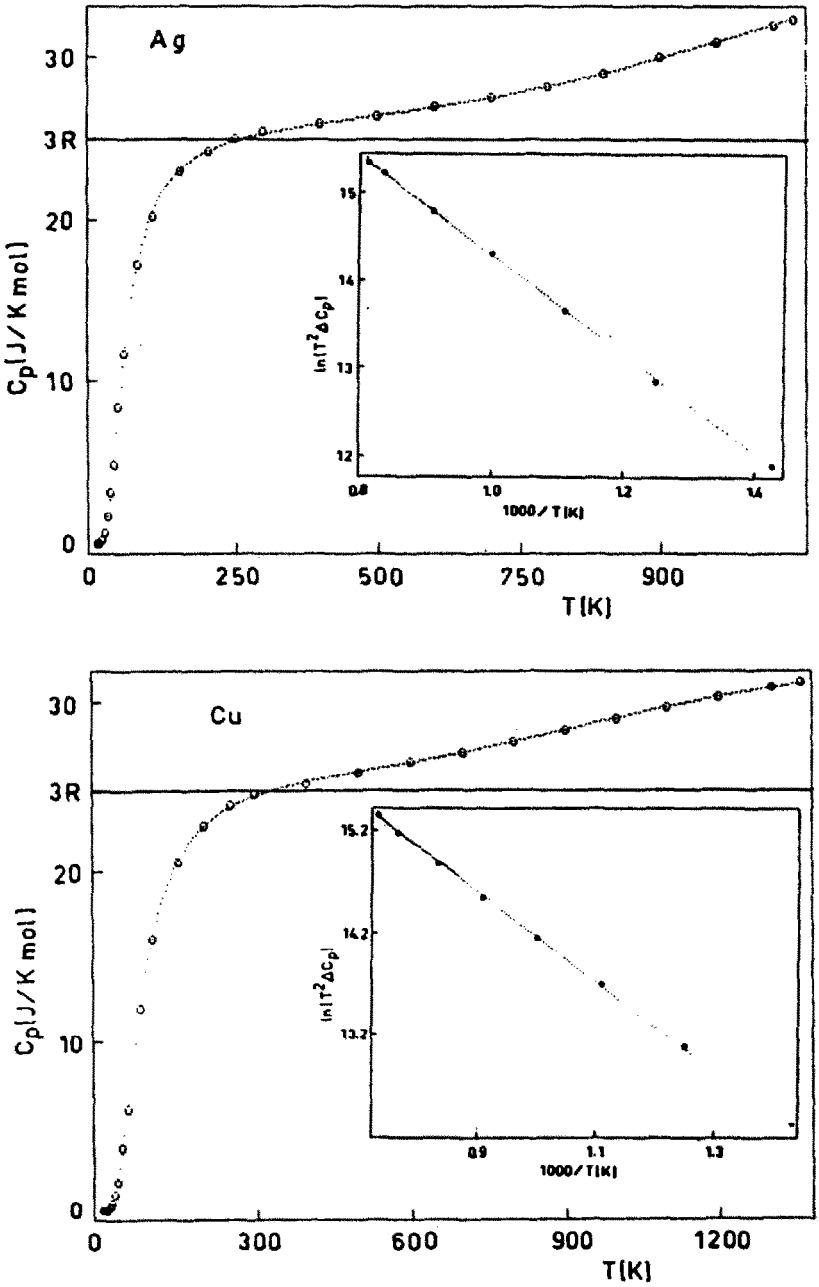


Fig. 1: Comparison of the C_p vs T data for Al, Au, Ag and Cu from Ref. 7 (open circles), with the values generated using Eq.1 (dotted line) and the parameters shown in Table I. The open circles in the inserts correspond to the C_p vs T data from which



the first two terms in the right hand side of Eq. 1 have been substracted out; while the dotted lines correspond to the third term in the right hand side of Eq. 1. In the case of gold the filled circles correspond to C_p vs T data collected from Ref. 1.

data for 0 < T < 5 K using Eq. 2, the values for γ and Θ_D are determined and shown in Table I, where also values reported by other authors are included to allow for a comparison. As may be seen the agreement between the values of γ and Θ_D determined in this work and those reported by other authors is quite good. Second, the values obtained for γ are substituted into Eq. 1, and this in turn used to determine T_{oD}, c_D, $A = R \exp(S_f/k)$ and E_f by fitting to the data over the whole temperature range, i.e. 0 < T < melting point. The parameters obtained are given in Table I, and the generated curves compared with the experimental data in Fig. 1. As may be seen in all cases the description provided by Eq. 1 of the data is excellent.

TABLE I. VALUES OBTAINED FOR THE VARIOUS PARAMETERS APPEARING IN EQS. 1 AND 2. (*)

	γ (10^{-6} J K^{-2} mol^{-1})	Θ_D (K)	T_{oD} (K)	c_D (10^{-5} K^{-1})	A (J K^{-1} mol^{-1})	E_f (10^3 K)
Al	1490 ± 10	421 ± 1	398 ± 1	11.11 ± 0.43	9.6 ± 0.5	3.49 ± 0.11
	1467[a]	446[a]				7.7 ± 0.3[c]
	780 ± 20	165 ± 1	175 ± 2	6.9 ± 1.0	4.28 ± 0.76	3.84 ± 0.34
Au	780 ± 20	165 ± 1	175 ± 2	8.72 ± 0.65	22.5 ± 5.4	6.70 ± 0.56
	729 ± 10[a]	162.5 ± 1.5[b]				11.3 ± 0.2[d]
Ag	653 ± 7	226 ± 1	214 ± 1	9.96 ± 0.40	13.8 ± 1.5	5.60 ± 0.28
	650 ± 5[b]	226 ± 1[b]				13.5 ± 0.3[d]
Cu	690 ± 2	345 ± 1	314 ± 1	7.74 ± 0.36	6.11 ± 0.33	4.45 ± 0.16
	695 ± 5[b]	344.5 ± 1.5[b]				15.2 ± 0.6[e]

* All the values without a superscript are deduced in this work as indicated in text. In all cases the data used is that of Ref. 7, except in the case of gold where the first line values for T_{oD}, c_D, A and E_f are deduced using the data reported in Ref. 1.

[a] Values taken from Ref. 17.

[b] Values taken from Ref. 6.

[c] Values taken from Refs. 11 and 12.

[d] Values taken from Refs. 13 and 14.

[e] Values taken from Refs. 15 and 16.

It may be mentioned that very similar values to those given in Table I are obtained by using other sets of C_p vs T data (6,9). The values deduced for T_{oD} differ from the corresponding Θ_D by less than 10%, which is a reasonable discrepancy to be expected (10). This is certainly not the case for the formation energy E_f, which are widely different from those obtained by

other techniques such as thermal expansion, positron annihilation, etc. This is a somewhat annoying situation which may be due to various causes. First, the high temperature data is quite scarce and following the case of gold (1,7) it would also seem that C_p vs T data near the melting point are not reliable. Second, it has been suggested that anharmonic effects should make an important contribution on approaching the melting point (18), although there are no solid proofs in this sense. Third, even though the values produced for E_f in this work are very different from those determined by other techniques, Eq. 1 has been successfully used in other cases (5,19,20) giving confidence to the analysis based on it.

It may be concluded by saying that although the C_p vs T data for the four fcc metals analysed in this work are not as reliable as would be desired on approaching the corresponding melting points, these unreliabilities are not enough as to explain the large discrepancies between the values determined for E_f in this work with those found by other authors. Therefore there is some other physical process which affects the C_p vs T data, and this gives a dominant contribution as compared to that of vacancies formation to the specific heat, which is not accounted for in Eq. 1. Although the origin of this physical process is not clear, it may be said that its mathematical description should be similar to that of vacancies formation whose main characteristic parameters are those deduced in this work and given in Table I under the headings A and E_f.

ACKNOWLEDGEMENTS

Partial financial support provided by Consejo Nacional de Investigaciones Cientificas y Tècnicas (CONICET) and by Consejo de Investigaciones Cientificas y Tecnològicas de la Provincia de Còrdoba (CONICOR), is gratefully acknowledged.

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