

Heat Capacity of Titanium between 4°K and 15°K*

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 (Received January 27, 1956)

The heat capacity of high-purity annealed titanium was determined in the temperature range 4 to 15°K. Results obtained can be represented by the equation $C/T(\text{joules/g atom deg}^2) = 3.38 \times 10^{-3} + 2.60 \times 10^{-5} T^2$ with an average deviation of 1.57%. From this γ , the electronic specific heat coefficient, and the Debye θ are evaluated to be $(3.38 \pm 0.04) \times 10^{-3}$ joule/g atom deg² and $421 \pm 2^\circ\text{K}$, respectively.

IN connection with a program for the study of the energetics of metallic systems at the University of Pittsburgh, the heat capacity of titanium has been measured from 4°K to 15°K. The calorimeter in which the measurements were carried out has the following features: (1) a gas thermometer is used as the working thermometer; (2) the sample is enclosed in the thermometer chamber so that the thermometric gas also serves as the heat exchange gas; (3) the calorimeter is surrounded by an adiabatic shield in order to minimize heat losses. A complete description of the apparatus and the experimental method will be published elsewhere.¹

The sample consisted of 384.39 grams or 8.029 gram atoms of crystal bar made by the Van Arkel process. Its purity was represented by the manufacturer to be 99.95 to 99.99%. The heat-capacity determinations were made in the following sequence: 16 measurements from 5.69°K to 15.55°K, five measurements from 3.95°K to 5.87°K, five measurements from 11.69°K to 14.29°K, and nine measurements from 6.35°K to 15.76°K. After the first 26 measurements the sample container-thermometer bulb was evacuated and a new quantity of thermometric gas introduced into the system. There was no systematic deviation in

measured heat capacity between different fillings. The temperature increments employed in the measurements were approximately 0.5 degree.

The unsmoothed data are listed in Table I and the plot of C/T versus T^2 is shown in Fig. 1. A least squaring procedure applied to the data below 13°K gave the following relationship:

$$C/T(\text{joules/g atom deg}^2) = 3.38 \times 10^{-3} + 2.60 \times 10^{-5} T^2.$$

This equation is represented as the straight line in Fig. 1. For 26 points below 13°K the average deviation between the measured heat capacity and the values computed from this equation is 1.57%.² From the above equation and the experimental scatter one evaluates γ , the electronic specific heat coefficient, to be $(3.38 \pm 0.04) \times 10^{-3}$ joule g atom⁻¹ deg⁻² and the Debye characteristic temperature to be $421 \pm 2^\circ\text{K}$. These values may be compared with those of Estermann, Goldman, and Friedberg³ who made measurements on a sample of titanium from approximately 2 to 4°K. They find that $\gamma = 3.35 \times 10^{-3}$ joule g atom⁻¹ deg⁻², in excellent agreement with the present results. Their value for θ , however, is 280°K which is considerably lower than the value found in this study. The variation in Debye θ may originate in differences in the chemical and physical states of the samples used. The sample used in the present work was of higher purity and was annealed in a helium atmosphere at 500°C for 3 hours before being studied. The measurements by

TABLE I. Heat capacity of titanium (unsmoothed data).

$T^\circ\text{K}$	$100C_p$ joules/deg g atom	$T^\circ\text{K}$	$100C_p$ joules/deg g atom
5.686	2.30	4.917	1.98
6.316	2.75	5.381	2.19
6.986	3.16	5.867	2.56
7.640	3.70	11.691	7.98
8.288	4.26	12.344	8.98
8.953	4.98	12.998	10.17
9.621	5.71	13.648	10.92
10.319	6.12	14.287	12.6
11.042	7.15	6.348	2.90
11.693	8.17	6.984	3.28
12.336	9.20	7.618	3.87
12.978	9.87	8.253	4.36
13.619	10.68	8.898	4.90
14.233	12.4	9.559	5.54
14.899	14.0	10.242	6.33
15.555	15.5	15.129	15.3
3.946	1.45	15.757	16.7
4.450	1.71		

* This research was supported by a grant from the National Advisory Committee for Aeronautics.

¹ Aven, Craig, and Wallace, Rev. Sci. Instr. (to be published).

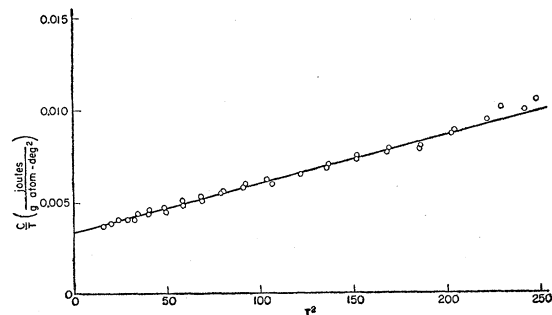


FIG. 1. C/T versus T^2 for titanium.

² These were first data obtained with the new calorimeter. In later experiments a precision of about 0.5% has been attained.
³ Estermann, Friedberg, and Goldman, Phys. Rev. **87**, 582 (1952).

Estermann *et al.* were made on a sample in the "as received" condition.⁴

The heat-capacity work of Kothen and Johnston⁵ at temperature above 15°K indicates a Debye θ for titanium in excess of 280°K but somewhat less than has been found in the present study. The values of θ computed from their measurements show a variation with temperature, as is generally the case, ranging from 354°K at 100°K to 360°K at 20°K. The trend with temperature is toward the higher value obtained

in this study. On the other hand, below 20°K the data of Kothen and Johnston lead to θ values which decrease with decreasing temperatures to a value of 335°K at 15.4°K, the lowest temperature studied. Thus the θ values in this range are tending toward the lower value of θ . However, the measurements of Kothen and Johnston are least reliable between 15 and 20°K and the θ values in this range are too uncertain for one to consider a trend to lower values to have been established. In fact, the data obtained in the present study over the upper limit of the measurement suggest just the contrary; namely, that at temperatures around 15°K, θ decreases with increasing temperature.

⁴ Dr. Friedberg (private communication).

⁵ C. W. Kothen and H. L. Johnston, *J. Am. Chem. Soc.* **75**, 3101 (1953).

Association Energy of Vacancies and Impurities with Edge Dislocations in NaCl†

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(Received January 3, 1956)

Calculations have been made of the energies of association of Sr⁺⁺ ions, Cd⁺⁺ ions, and positive-ion vacancies with the core of a (110) edge dislocation in NaCl. It is found that the vacancy has an association energy of 0.4 ev, but that other impurities have smaller association energies. On the basis of this energy of association, the numbers of vacancies and divalent ion-vacancy complexes pinned in the cores of the (110) edge dislocations in a well-annealed crystal were calculated. These numbers are large enough at room temperature to suggest that impurity and vacancy pinning might be the agent determining the critical yield stress in annealed NaCl. The elastic field interaction between point defects and a dislocation is tabulated and compared with the interaction obtained within the core. It is shown that the elastic energy of interaction does not necessarily project into the core in a smooth fashion, but that in the case of the vacancy, an elastically "large" inclusion behaves like a "small" inclusion in the core. Several possible suggestions are made which may explain the strong hardening effect of divalent impurity additions to NaCl.

I. INTRODUCTION

IN this paper we shall discuss some aspects of the association of vacancies and various types of impurities with the active edge dislocations in NaCl. Since it is found that NaCl glides most easily in the [110] direction on (110) planes, the edge dislocations with [110] Burgers vectors and (110) slip planes are the active dislocations.¹ It is found that NaCl will also glide on (100) planes under certain conditions, but we have not discussed the dislocations responsible for such flow in detail.

In a model due to Cottrell,² impurity atoms are attached to a dislocation because the misfit of the impurity in the lattice may be relaxed somewhat by the strained region around a dislocation. In cases where the major misfit is due to a simple difference in size between the impurity and lattice atoms, there is an interaction with edge dislocations. In other cases, the

misfit is due to the wrong "shape" of the impurity, and there is an interaction with screw dislocations.³ Perhaps the two greatest successes of the model are the prediction of the sharp yield point observed in some systems, and the dependence of the yield point on temperature.⁴

Most of the work on dislocation pinning has been concerned with metals. However, there are several respects in which the alkali halides are of special interest. First, it is obvious that the theoretical discussion of the core of a dislocation in a metal is very difficult because the law of force between the atoms is quite complicated. In the alkali halides, on the other hand, there has been a history of successful attack on various problems involving atomic forces by use of the simple Born-Mayer central force ionic theory. Mott and Littleton⁵ calculated the energy of formation of a Schottky defect in these crystals. Impurities have been treated by Reitz and Gammel,⁶ Bassani and Fumi,⁷ and

† This research has been supported by the Office of Naval Research and the U. S. Air Force.

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¹ E. Schmid and W. Boas, *Plasticity of Crystals* (Hughes and Company, London, 1950).

² A. H. Cottrell and B. A. Bilby, *Proc. Phys. Soc. (London)* **A62**, 49 (1949).

³ C. Crussard, *Métaux et corrosion* **25**, 203 (1950).

⁴ D. S. Wood and D. S. Clark, *Proc. Am. Soc. Testing Materials* **49**, 717 (1949).

⁵ N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

⁶ J. R. Reitz and J. L. Gammel, *J. Chem. Phys.* **19**, 894 (1951).

⁷ F. Bassani and F. G. Fumi, *Nuovo cimento* **11**, 274 (1954).