

## Specific Heat of Tellurium and Selenium at Very Low Temperature

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# Specific Heat of Tellurium and Selenium at Very Low Temperatures\*

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## Synopsis

The specific heat of tellurium and selenium was measured in the range of liquid helium temperatures. The measurements were made with a calorimeter of Nernst-Eucken's type. A carbon composition resistor, having a nominal room-temperature resistance of ten ohms, was used as the suitable thermometer in this temperature region. It was found that the observed values of the specific heat of these metals did not consist of the electronic specific heat but only of the lattice one which is proportional to  $T^3$ . Discussions were given of the specific heat of these metals at low temperatures from the viewpoint of the anisotropy of the chain-like crystal lattice.

## I. Introduction

Considerable attention has recently been given to the vibrational spectrum and thereby to the specific heat of the lattice of an anisotropic crystal. Owing to its layered structure, graphite is a typical example of the anisotropic crystal that consists of atomic planes within which each atom is strongly bound together in a hexagonal network, the planes themselves being held together by a weak attraction of the van der Waals' type. The lattice contribution to the specific heat<sup>(1)(2)</sup> has been found to be proportional to  $T^2$  at low temperatures instead of being consistent with the usual Debye's theory. Such  $T^2$  dependence of the specific heat has also been found in other layered crystals, such as gallium<sup>(3)</sup>, antimony<sup>(4)</sup>, and boron nitride<sup>(5)</sup>. Such behaviour of the specific heat has already been explained by the semi-empirical formula of Tarasov and De Sorbo<sup>(6)</sup>, and especially in the case of graphite, considerable theoretical studies have been made by Komatsu and Nagamiya<sup>(7)</sup>, Krumhansl and Brooks<sup>(8)</sup>, Gurney<sup>(9)</sup> and Rosenstock<sup>(10)</sup>. However, it is questionable whether the  $T^2$  dependence holds good even at temperature as low as 0°K or such a dependence will break at some very low temperature, below which the specific heat becomes proportional to  $T^3$ . According to recent

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\* The 837th report of the Research Institute for Iron, Steel and Other Metals.

(1) W. De Sorbo and W. W. Tyler, *J. Chem. Phys.*, **21** (1953), 1660.

(2) U. Bergenlid, R. W. Hill, F. J. Webb and J. Wilks, *Phil. Mag.*, **45** (1954), 851.

(3) W. De Sorbo, *J. Chem. Phys.*, **21** (1953), 168.

(4) W. De Sorbo, *Acta Met.*, **1** (1953), 503.

(5) A. S. Dworkin, D. J. Sasmor and E. R. Van Artsdalen, *J. Chem. Phys.*, **22** (1954), 837.

(6) W. De Sorbo, *Acta Met.*, **2** (1954), 274.

(7) K. Komatsu and T. Nagamiya, *J. Phys. Soc. Japan*, **6** (1951), 438.

(8) J. Krumhansl and H. Brooks, *J. Chem. Phys.*, **21** (1953), 1663.

(9) R. W. Gurney, *Phys. Rev.*, **88** (1952), 465.

(10) H. B. Rosenstock, *J. Chem. Phys.*, **21** (1953), 2064.

observations<sup>(2)(11)(12)</sup>, the change from  $T^2$  dependence to  $T^3$  one with decreasing temperature was found. Komatsu<sup>(13)</sup> extended his previous analysis<sup>(7)</sup> and obtained results which agreed with the measurement of Bergenlid, Hill, Webb, and Wilks<sup>(2)</sup>. However, from the recent work by Keesom and Pearlman<sup>(12)</sup>, another analysis also became possible, including that of the electronic specific heat which could not be found by the former analysis. Therefore, in the present state, this problem cannot be said to have been settled quantitatively.

There is another group of crystal anisotropy, i. e., the chain-like structure<sup>(14)</sup> to which tellurium and selenium belong. The atoms occupying the lattice points have only two nearest neighbours and are bound to make continuous chains by virtue of main valence force. These chains lie at the edges of unit cells and the

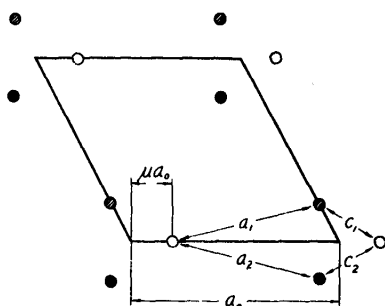


Fig. 1. Crystal structure of tellurium and selenium. The mark  $\circ$  lies in the same plane,  $\circ$  in the plane of height of  $\frac{1}{3}c_0$  and  $\bullet$  in the plane of height of  $\frac{2}{3}c_0$  from the plane of  $\circ$ . A spiral makes a round through  $\circ$ ,  $\circ$ , and  $\bullet$ .

interaction between them is weak owing to van der Waals' force. The arrangement of atoms viewed from the direction parallel to the chain axis (c-axis) is shown in Fig. 1. The distance between two neighbouring chains,  $a_0$ , is 4.44Å in tellurium and 4.34Å in selenium. The shortest distance between two tellurium atoms,  $c_1$ , is 2.86Å and that between two selenium atoms is 2.32Å. The nearest approach of

two atoms in the adjacent chains,  $a_1$ , is 3.46Å in both metals. These lattice parameters together with others are listed in Table 1. The specific heat of tellurium down to liquid hydrogen temperature was measured by Anderson<sup>(15)</sup>, and Slansky and Coulter<sup>(16)</sup> and that of selenium by Anderson<sup>(15)</sup> and De Sorbo<sup>(17)</sup>. The specific heat of these metals has been worked out by Tarasov and De Sorbo<sup>(6)</sup>, by considering the interaction between chains, in addition to the one-dimensional Debye's type vibration in the chain. In this way, they explained the results of observations by using a semi-empirical expression which contains two characteristic temperatures,

Table 1. Table of lattice parameters. (Å unit)

|    | $c_1$ | $c_2$ | $c_0$ | $a_1$ | $a_0$ | $a_2$ | $\mu$ |
|----|-------|-------|-------|-------|-------|-------|-------|
| Se | 2.32  | 3.68  | 4.95  | 3.46  | 4.34  | 4.49  | 0.217 |
| Te | 2.86  | 4.45  | 5.90  | 3.46  | 4.44  | 4.85  | 0.269 |

- (11) F. J. Webb and J. Wilks, Proc. Roy. Soc., **A230** (1955), 549.  
 (12) P. H. Keesom and N. Pearlman, Phys. Rev., **99** (1955), 1119.  
 (13) K. Komatsu, J. Phys. Soc. Japan, **10** (1955), 346.  
 (14) R. W. G. Wyckoff, *The Structure of Crystals*, 2nd Ed., (1931), p. 203.  
 (15) C. T. Anderson, J. Am. Chem. Soc., **59** (1937), 1036.  
 (16) C. M. Slansky and L. V. Coulter, J. Am. Chem. Soc., **61** (1939), 564.  
 (17) W. De Sorbo, J. Chem. Phys., **21** (1953), 1144.

$\theta_1$  and  $\theta_3$ . From this expression, it may be expected that at very low temperatures the specific heat of these metals should be proportional to  $T^3$ . However, inasmuch as the measurement in liquid helium range has never been made, it will be interesting to know whether such  $T^3$  law really will hold and what mode of lattice vibration will bring forth such a specific heat.

Stockmayer and Hecht<sup>(18)</sup> studied the specific heat of a chain-like polymeric crystal by modifying the calculation by Blackman<sup>(19)</sup> for the lattice vibration of the simple cubic crystal. But their results differ from the behaviour of specific heat of the metals in question. Recently, Yoshimori<sup>(20)</sup> tried to calculate the specific heat on the actual lattice of the chain-like crystal by considering interactions between the nearest neighbours in a chain and between every chains. It is shown from this calculation that the specific heat of such a crystal may be explained by assuming suitable values for three elastic constants.

There are two advantages in investigating the specific heat of the lattice vibration of anisotropic crystals by using tellurium and selenium. The first, graphite, which was extensively studied as mentioned above, is apt to adsorb various gases especially at low temperatures, to desorb them in course of observation of the specific heat, to cool itself due to the heat of desorption and to yield erroneous results. The second is that these metals being semiconductors, the specific heat of electrons is almost negligible compared with that of lattice, owing to the very small contribution of conduction electrons. Therefore, in the present case, these metals were selected to study the specific heat of lattice of the anisotropic crystal at very low temperatures.

## II. Experiments

### 1. Specimen

The tellurium specimen was cylindrical, about 1.4 cm in diameter, 7.9 cm in length and 61.68 grams in weight; it was refined by repeating the vacuum fractional distillations as described in the previous paper<sup>(21)</sup>. The selenium specimen of the same form, about 2.0 cm in diameter, 5.0 cm in length and 68.10 gram in weight, was purified similarly. As selenium has an amorphous phase, this sample was transformed into the hexagonal one by heat-treatment in vacuo at about 125°C for 72 hours. An X-ray photograph of this transformed material showed a hexagonal pattern. It seemed to be sure that both specimens were extremely pure. A longitudinal hole was bored in each specimen through the center of the cylinder, in order to insert a carbon-composition resistor made by Allen-Bradley Co. (1/4 watt, 10 ohms at room temperature) as a suitable thermometer in liquid helium range, the resistance change of which is given by Clement and Quinnell<sup>(22)</sup>, and Boorse,

(18) W. H. Stockmayer and C. E. Hecht, *J. Chem. Phys.*, **21** (1953), 1954.

(19) M. Blackman, *Proc. Roy. Soc.*, **A148** (1935), 384; **A159** (1937), 416.

(20) A. Yoshimori, Private communication.

(21) T. Fukuroi, S. Tanuma and S. Tobisawa, *Sci. Rep. RITU*, **A1** (1949), 365.

(22) J. R. Clement and E. H. Quinnell, *Rev. Sci. Instr.*, **23** (1952), 213.

Zemansky, and Brown<sup>(23)</sup>. It was calibrated between 1.5 and 4.5°K by comparing the empirical relation obtained by Clement and Quinnell and the 1948 temperature scale<sup>(24)</sup>. A constantan wire wound non-inductively on the specimen was used as the heater. It was thermally bonded to and electrically insulated from the specimen by means of glyptal lacquer. The heat capacity of the glyptal, heater and thermometer, etc., was less than one per cent of the total and thus could be neglected.

## 2. Apparatus

The calorimeter used in this experiment, which belongs to Nernst and Eucken's type, is shown schematically in Fig. 2. *A* is a tube of nickel-copper alloy (Ni 10 per cent and Cu 90 per cent), 0.6 cm in diameter; *B* and *F* are two brass cans,

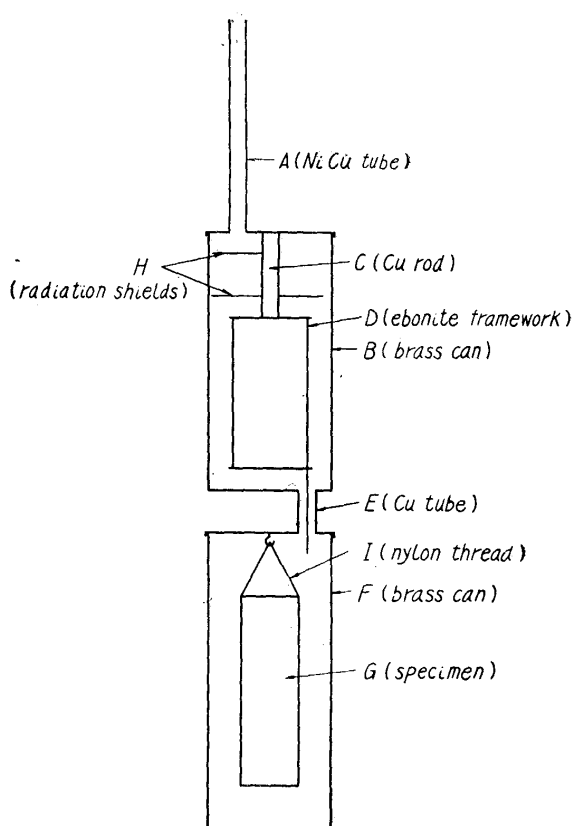


Fig. 2. The apparatus.

4.5 cm in diameter and 13 cm in length; *C* the copper rod, 1 cm in diameter and 5 cm in length; and *E* the copper pipe, 1 cm in diameter, through which *F* is connected to *B*. *D* is a framework made of ebonite and *H* is two radiation shields. Through the pipe *A*, *B* and *F* are evacuated and electrical lead wires are taken out to the measuring circuit. Two sets of four leads of the enamelled copper wire (No. 42 gauge), having lengths of 6 meters each are provided for the thermometer and heater, respectively. The upper half of these wires was tied rounds on *C* and thermally bonded by glyptal. The lower half of the wires was loosely wound on *D* with a view to making the heat path longer before they are connected with the heater and the thermometer.

The specimen *G* was hung with nylon threads *I* in a vacuum can *F*, and the vacuum of the order of  $10^{-6}$  mm Hg was maintained by using two Hickman pumps backed by an oil rotary pump.

## 3. Method of measurement

The rate of energy dissipation in the heater was determined by measuring the current through it and its resistance. In measuring the heat capacity, the resistance of the thermometer was observed by galvanometer deflection every 30 seconds. After the temperature drift,  $dR/dt$ , became constant, the heating current

(23) H. A. Boorse, M. W. Zemansky and C. M. Brown, *Phys. Rev.*, **84** (1951), 1050.

(24) H. van Dijk and D. Shoenberg, *Nature*, **164** (1949), 151.

was switched on. The usual heating periods ranged from 15 to 30 seconds. During the heating period, the galvanometer deflection was observed every 5 seconds. Thereafter,  $dR/dt$  was again observed for two or three minutes. When it became steady again for some duration, the observation was repeated. The specific heat was calculated by the Leiden's procedure<sup>(25)</sup>. The temperature rise during a heating period usually ranged from 0.01 to 0.1°.

### III. Results

Experiments were carried out from 1.5 to 4.5°K with specimens of tellurium and selenium. To compare the experimental results with the theory, it is necessary to convert the measured value into the specific heat at constant volume,  $C_v$ , as the former is the specific heat at constant pressure,  $C_p$ . However, at such very low temperatures, it may be permissible to take  $C_p$  for  $C_v$  because of the smallness of the difference between them.

#### 1. Tellurium

Observations were made six times, and the results are given in Table 2 and Fig. 3. In Table 2, the temperature given in the first column is the average of each measurement and  $T$  in the second column is the rise in temperature observed.

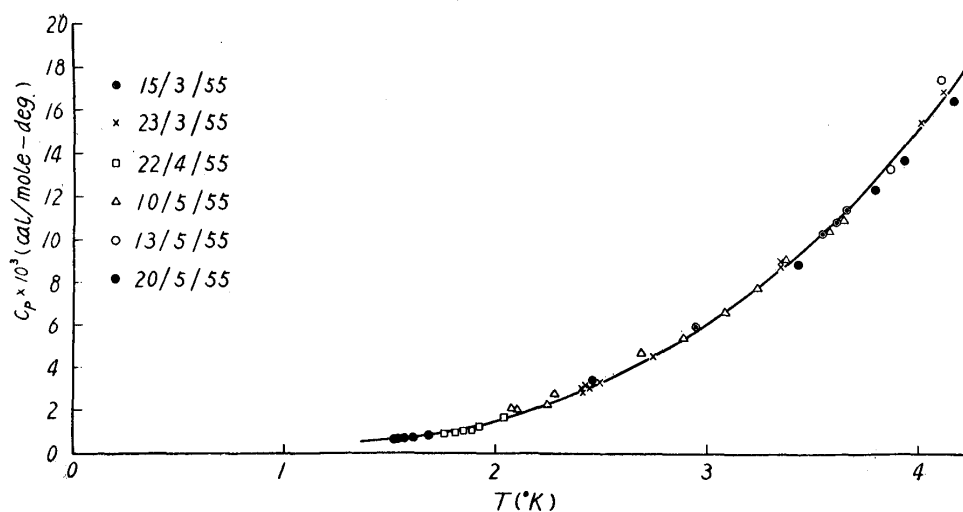


Fig. 3. Specific heat of tellurium between 4.2 and 1.5°K.

In Fig. 4,  $\log C_v$  versus  $\log T$  curve is plotted. The points below 5°K show the present measurements, while the values above liquid hydrogen temperature are those by Slansky and Coulter<sup>(16)</sup>, and Anderson<sup>(15)</sup>. The smooth change of this curve can be seen without any anomaly. Fig. 5 shows the relation between  $C_v/T$  and  $T^2$ . Though there are some irregularities, this curve may be regarded as a straight line through the origin, indicating the absence of electronic contribution. Thus, the specific heat of tellurium in this range of temperature is proportional to  $T^3$ .

(25) W. H. Keesom and J. A. Kok, Leiden Comm., 219 (c).

This is also shown in Fig. 4, in which the observed slope below 5°K is proportional to  $T^3$ . From these results, the usual Debye's temperature can be calculated as follows :

$$\theta_D = 128.8 \pm 0.5^\circ\text{K}.$$

Table 2. Atomic heat of tellurium.

| Date    | No. | T<br>(°K) | $\Delta T$<br>(deg.) | $C_p$<br>( $10^{-3}$ cal/mole deg.) |
|---------|-----|-----------|----------------------|-------------------------------------|
| 15/3/55 | 1   | 2.462     | 0.1183               | 3.487                               |
| "       | 2   | 2.947     | 0.0784               | 6.020                               |
| "       | 3   | 3.554     | 0.0512               | 10.39                               |
| "       | 4   | 3.615     | 0.1429               | 10.90                               |
| "       | 5   | 3.660     | 0.0622               | 11.49                               |
| 23/3/55 | 1   | 2.404     | 0.0755               | 3.035                               |
| "       | 2   | 2.412     | 0.0756               | 2.928                               |
| "       | 3   | 2.424     | 0.0722               | 3.210                               |
| "       | 4   | 2.435     | 0.0652               | 3.128                               |
| "       | 5   | 2.492     | 0.0683               | 3.398                               |
| "       | 6   | 2.742     | 0.0464               | 4.668                               |
| "       | 7   | 3.345     | 0.0755               | 9.135                               |
| "       | 8   | 3.353     | 0.0761               | 8.875                               |
| "       | 9   | 4.015     | 0.0844               | 15.58                               |
| "       | 10  | 4.118     | 0.0883               | 17.01                               |
| 22/4/55 | 1   | 1.757     | 0.0675               | 0.935                               |
| "       | 2   | 1.809     | 0.0995               | 1.071                               |
| "       | 3   | 1.857     | 0.0962               | 1.137                               |
| "       | 4   | 1.891     | 0.0959               | 1.164                               |
| "       | 5   | 1.926     | 0.0850               | 1.280                               |
| "       | 6   | 2.040     | 0.0603               | 1.778                               |
| 10/5/55 | 1   | 2.075     | 0.0495               | 2.161                               |
| "       | 2   | 2.106     | 0.0480               | 2.156                               |
| "       | 3   | 2.245     | 0.0448               | 2.341                               |
| "       | 4   | 2.278     | 0.0901               | 2.853                               |
| "       | 5   | 2.691     | 0.1536               | 4.753                               |
| "       | 6   | 2.887     | 0.1335               | 5.433                               |
| "       | 7   | 3.088     | 0.1095               | 6.709                               |
| "       | 8   | 3.241     | 0.1979               | 7.804                               |
| "       | 9   | 3.370     | 0.1701               | 9.198                               |
| "       | 10  | 3.582     | 0.1482               | 10.49                               |
| "       | 11  | 3.653     | 0.1405               | 10.99                               |
| 13/5/55 | 1   | 3.872     | 0.1961               | 13.36                               |
| "       | 2   | 4.113     | 0.1746               | 15.61                               |
| 20/5/55 | 1   | 3.433     | 0.0795               | 8.919                               |
| "       | 2   | 3.804     | 0.0575               | 12.43                               |
| "       | 3   | 3.943     | 0.0535               | 13.80                               |
| "       | 4   | 4.173     | 0.0437               | 16.57                               |
| "       | 5   | 1.529     | 0.0801               | 0.717                               |
| "       | 6   | 1.544     | 0.0963               | 0.729                               |
| "       | 7   | 1.566     | 0.0897               | 0.772                               |
| "       | 8   | 1.602     | 0.0907               | 0.764                               |
| "       | 9   | 1.682     | 0.0782               | 0.886                               |

Table 3. Atomic heat of selenium.

| Date     | No. | T<br>(°K) | $\Delta T$<br>(deg.) | $C_p$<br>( $10^{-3}$ cal/mole deg.) |
|----------|-----|-----------|----------------------|-------------------------------------|
| 17/9/55  | 1   | 2.632     | 0.0738               | 2.336                               |
| "        | 2   | 2.668     | 0.0561               | 2.925                               |
| "        | 3   | 2.984     | 0.0536               | 3.845                               |
| "        | 4   | 3.258     | 0.0655               | 4.961                               |
| "        | 5   | 3.286     | 0.1547               | 5.060                               |
| "        | 6   | 4.072     | 0.0798               | 9.424                               |
| "        | 7   | 4.239     | 0.0714               | 10.86                               |
| "        | 8   | 4.274     | 0.0663               | 11.55                               |
| 30/9/55  | 1   | 2.042     | 0.0337               | 1.054                               |
| "        | 2   | 2.121     | 0.0271               | 1.337                               |
| "        | 3   | 2.508     | 0.0378               | 1.861                               |
| "        | 4   | 3.496     | 0.0587               | 5.872                               |
| "        | 5   | 3.519     | 0.0745               | 5.590                               |
| "        | 6   | 3.954     | 0.0455               | 7.504                               |
| "        | 7   | 4.233     | 0.1270               | 9.919                               |
| "        | 8   | 4.423     | 0.1203               | 11.30                               |
| "        | 9   | 4.575     | 0.0954               | 13.20                               |
| 1/12/55  | 1   | 2.054     | 0.0175               | 1.055                               |
| "        | 2   | 2.308     | 0.0118               | 1.565                               |
| "        | 3   | 2.433     | 0.0271               | 1.903                               |
| "        | 4   | 2.531     | 0.0238               | 2.002                               |
| "        | 5   | 2.579     | 0.0277               | 2.321                               |
| "        | 6   | 2.543     | 0.0249               | 2.047                               |
| "        | 7   | 3.223     | 0.0147               | 4.266                               |
| "        | 8   | 3.479     | 0.0089               | 5.794                               |
| "        | 9   | 3.556     | 0.0116               | 5.805                               |
| "        | 10  | 3.803     | 0.0074               | 6.969                               |
| 9/12/55  | 1   | 1.730     | 0.0189               | 0.617                               |
| "        | 2   | 1.832     | 0.0847               | 0.714                               |
| "        | 3   | 1.890     | 0.0862               | 0.827                               |
| "        | 4   | 1.974     | 0.0742               | 1.000                               |
| "        | 5   | 2.089     | 0.0539               | 1.363                               |
| "        | 6   | 1.930     | 0.0571               | 0.941                               |
| "        | 7   | 1.964     | 0.0589               | 0.900                               |
| "        | 8   | 2.005     | 0.0516               | 1.042                               |
| "        | 9   | 2.056     | 0.0590               | 1.231                               |
| "        | 10  | 2.104     | 0.0531               | 1.409                               |
| "        | 11  | 2.238     | 0.0447               | 1.672                               |
| "        | 12  | 2.295     | 0.0460               | 1.626                               |
| "        | 13  | 2.406     | 0.0380               | 1.968                               |
| "        | 14  | 2.475     | 0.0338               | 2.125                               |
| "        | 15  | 2.667     | 0.0260               | 2.763                               |
| "        | 16  | 2.981     | 0.0190               | 3.819                               |
| "        | 17  | 3.146     | 0.0175               | 4.229                               |
| "        | 18  | 3.648     | 0.0287               | 6.924                               |
| "        | 19  | 3.858     | 0.0521               | 8.129                               |
| 23/12/55 | 1   | 2.318     | 0.0343               | 1.580                               |
| "        | 2   | 2.705     | 0.0204               | 2.380                               |
| "        | 3   | 2.757     | 0.0192               | 2.664                               |
| "        | 4   | 3.130     | 0.0129               | 3.965                               |
| "        | 5   | 3.479     | 0.0098               | 5.162                               |
| "        | 6   | 4.064     | 0.0089               | 8.694                               |

2. Selenium

The results observed from five runs are given in Table 3. Fig. 6 illustrates  $C_v/T$  versus  $T^2$  relation, which is represented by a straight line through the origin. Therefore, the specific heat of selenium is also proportional to  $T^3$ , having no electronic contribution, and the Debye's temperature is

$$\theta_D = 151.7 \pm 0.4^\circ\text{K}.$$

$\log C_v$  versus  $\log T$  curve is shown in Fig. 7, including the data by De Sorbo down to liquid hydrogen temperatures as well as the present data in liquid helium range. From this figure, it is also clear that the measured specific heat is proportional to  $T^3$  at very low temperatures.

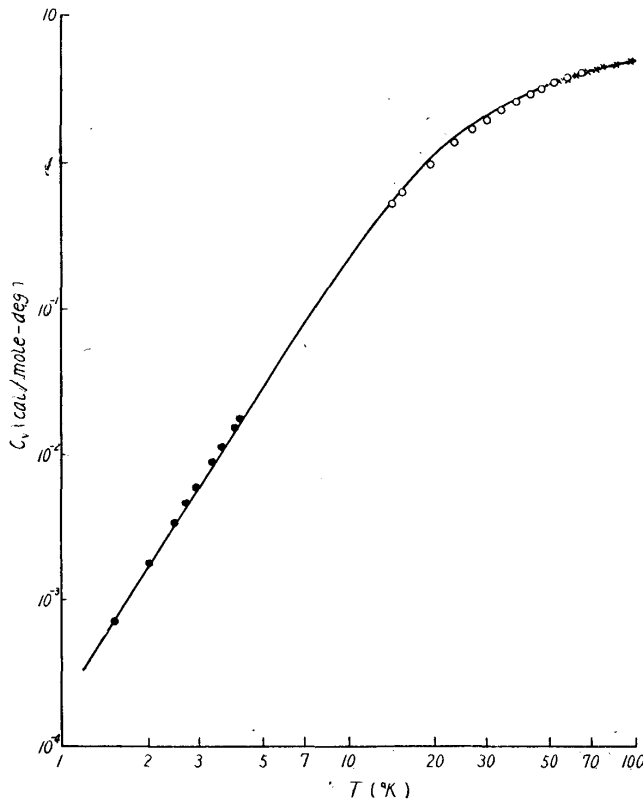


Fig. 4.  $\log C_v$  versus  $\log T$  curve for tellurium. ● our data, ○ Slansky and Coulter's data, × Anderson's data, and — is the calculated curve by Yoshimori.

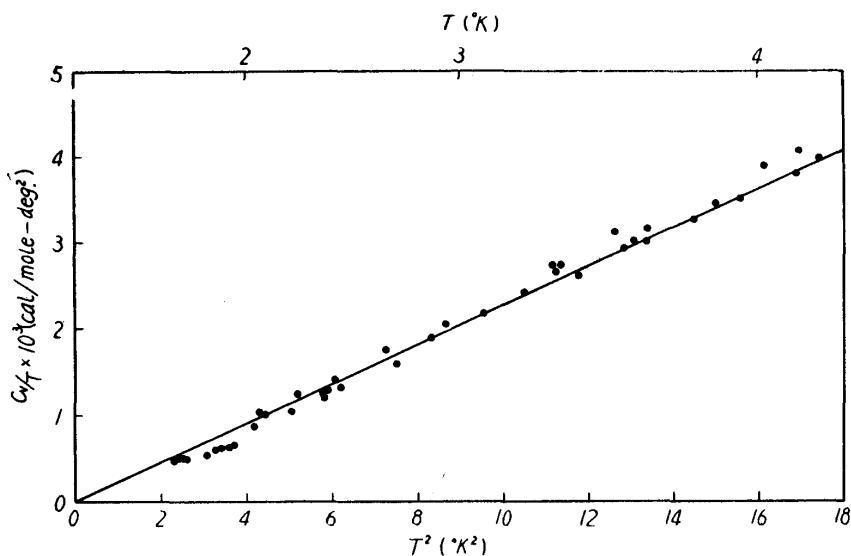
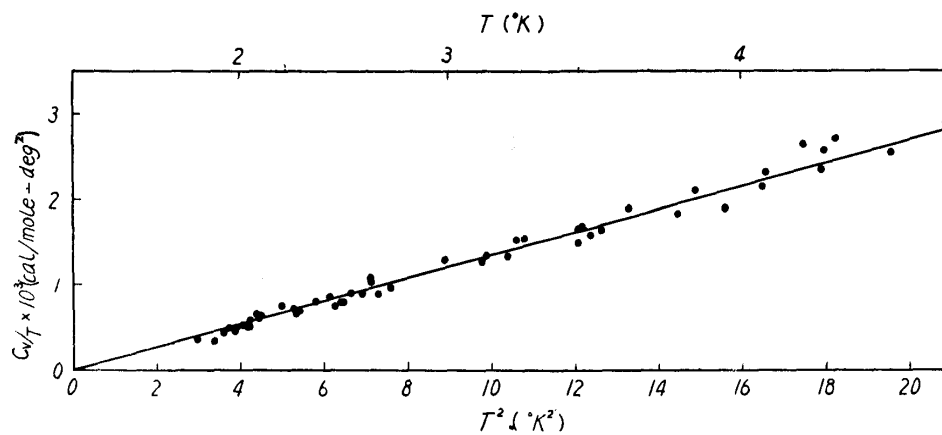
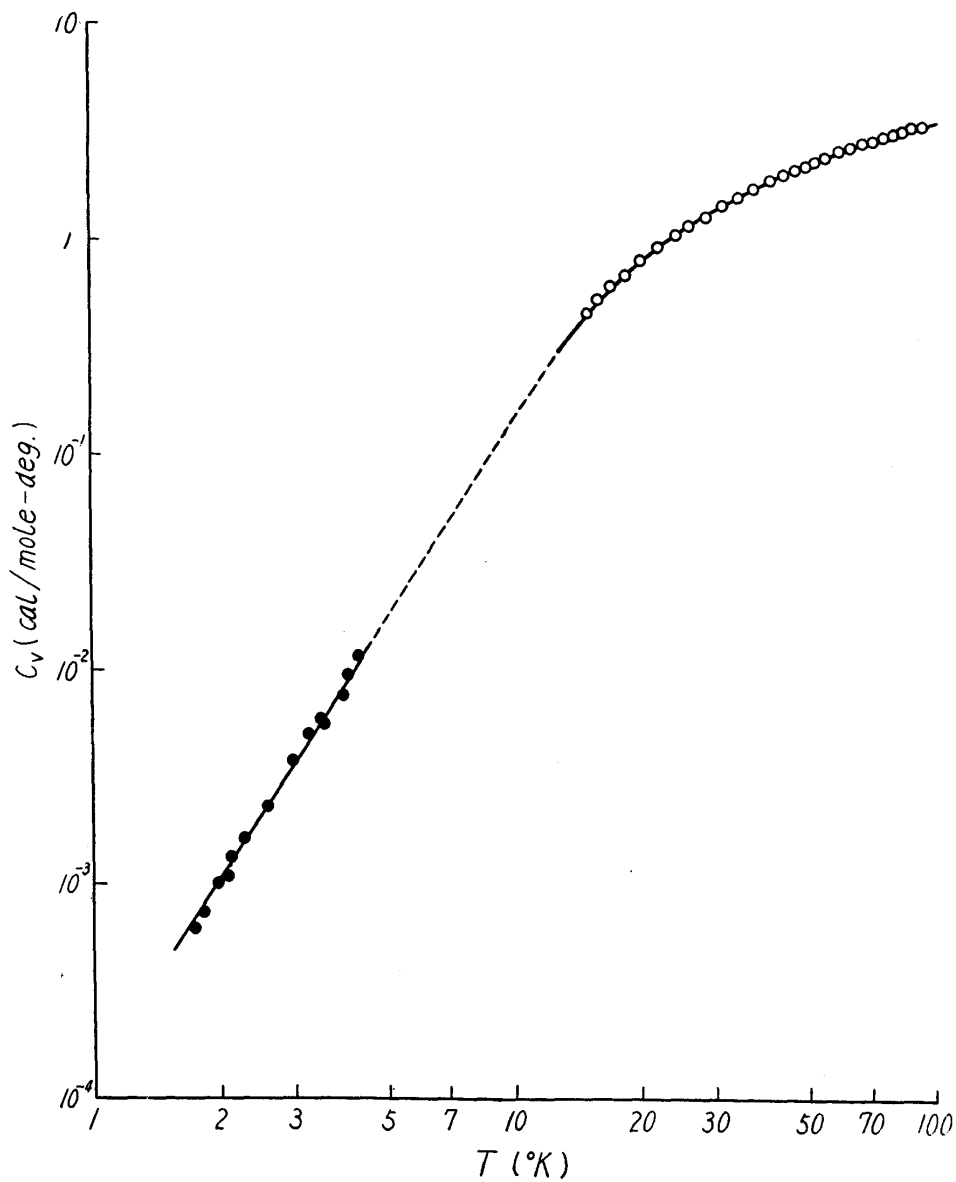


Fig. 5.  $C_v/T$  versus  $T^2$  curve for tellurium.

IV. Discussions

Generally speaking, the specific heat of a metal at very low temperatures consists of two parts; one is the specific heat of the lattice vibration and the other is of the electronic origin. In accordance with the convention, by plotting  $C_v/T$  against  $T^2$ , a straight line through the origin is obtained for both metals. Hence,



Fig. 6.  $C_v/T$  versus  $T^2$  curve for selenium.Fig. 7.  $\log C_v$  versus  $\log T$  curve for selenium.  
● our data, ○ De Sorbo's data.

it can be seen that the specific heat of these metals is proportional to  $T^3$  and has no linear term of  $T$ . In other words, the specific heat has no electronic contribution. These metals, being semiconductors, have very few conduction electrons or holes at very low temperatures. The result just mentioned may be considered to be most reasonable.

Hence, it appears that the  $T^3$ -relationship in the present case signifies the validity of the ordinary three-dimensional Debye's model. Even though some behaviour different from the Debye's type had been observed in the region of temperatures of several tens degrees absolute, the specific heat of anisotropic metals is proportional to  $T^3$  at very low temperatures. Such a behaviour may be explained by the following consideration. The low frequency wave rather than the high frequency one is mainly effective at very low temperatures, because the frequency which contributes chiefly to the specific heat is in the order of  $h\nu \sim kT$ . Then, as the crystal can be regarded as a continuum and the wave as a macroscopic elastic wave, the vibrational spectrum will become proportional to  $\nu^2$  at low frequency and consequently, the  $T^3$ -relationship will follow. Yoshimori<sup>(20)</sup>, however, remarked that  $3N$  freedoms in Debye's theory change to  $N$  freedoms at very low frequency in the chain-like crystal, because the high frequency branch becomes the optical mode, and therefore, are not effective at very low temperatures.

Recently, Tarasov and De Sorbo<sup>(6)</sup> have presented the following expression to represent the specific heat of the chain-like crystal, by using two characteristic temperatures  $\theta_1$  and  $\theta_3$ :

$$C_v = 3R(T/\theta_1) \int_0^{\theta_1/T} \frac{x^2 e^x}{(e^x - 1)^2} dx - (\theta_3/\theta_1) \left[ \frac{3RT}{\theta_3} \int_0^{\theta_3/T} \frac{x^2 e^x}{(e^x - 1)^2} dx - \frac{9RT}{\theta_3^3} \int_0^{\theta_3/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \right]$$

$$= D_1(\theta_1/T) - \theta_3/\theta_1 [D_1(\theta_3/T) - D_3(\theta_3/T)],$$

in which  $D_1$  is the specific heat function for one dimensional model and  $D_3$  is the usual Debye's function. In terms of this formula, the specific heat of tellurium and selenium down to liquid hydrogen temperatures can be expressed by assuming two suitable values for  $\theta_1$  and  $\theta_3$ . Their values are listed in Table 4. At very low temperatures, the above formula becomes

$$C_v = \frac{12}{5} \pi^4 R \frac{T^3}{\theta_1 \cdot \theta_3^2},$$

so that the  $T^3$ -law is obeyed. When the above values of  $\theta_1$  and  $\theta_3$ , however, are used in this equation, the values of  $C_v$  do not coincide with the present results. It is, therefore, necessary to modify  $\theta_3$  into  $\theta_3'$ , as shown in Table 4, to make it consistent.

Table 4. Table of characteristic temperatures.

|    | $\theta_D$ | $\theta_\tau$ | $\theta_1$ | $\theta_3$ | $\theta_3'$ |
|----|------------|---------------|------------|------------|-------------|
| Te | 128.8      | 89.3(90.8)    | 245        | 95         | 93          |
| Se | 151.7      | 105.2         | 370        | 75         | 97          |

where  $\theta_{\tau\text{Te}} = (90.8)$  is the value adopted by Yoshimori in his calculation.

The vibrational spectrum and the lattice heat of the chain-like crystal have been worked out by Yoshimori<sup>(20)</sup>. He studied the vibrational spectrum of the lattice of tellurium and selenium and tried to find the specific heat of tellurium below 100°K. His calculation is based on the following three assumptions for potential energy: (1) the potential energy for the change of the distance between neighbouring atoms in a chain is  $\kappa/2 \cdot (\Delta l)^2$ , (2) that for the change of the valence angle is  $\mu/2 \cdot (l \cdot \Delta \varphi)^2$  and (3) that for the change of the distance between the nearest atoms in the adjacent chains is  $\tau/2 (\Delta b)^2$ , where  $l$  and  $b$  are distances and  $\varphi$  is the valence angle between the corresponding atoms. He also assumed  $\kappa \gg \mu \gg \tau$ . The unit cell of tellurium contains three atoms, so there appear nine branches of the normal modes which are divided into three groups, (A), (B), and (C). (A) is the optical mode of the high frequency related to  $\kappa$ . (B) is the optical one of the low frequency, which is resulted from the torsional vibration of the chain and is related to  $\mu$ . This mode gives rise to  $f(\nu) = \text{constant}$  and, then, the specific heat becomes proportional to  $T$ . (C) is the acoustical mode which is related to  $\tau$ . This mode gives a three-dimensional vibration in which  $T^3$ -law is valid, though the anisotropy of sound velocity appears. Since there is no reliable data on  $\kappa$ ,  $\mu$ , and  $\tau$ , these constants must be determined by fitting the experimental results. Then, taking the total number of acoustic mode as  $N$ ,  $\theta_\tau$  is derived from the present data and then  $\tau$  is obtained from it by neglecting the anisotropy of sound velocity.  $\kappa$  and  $\mu$  are determined from the data above 100°K. That is,

$$\begin{aligned}\kappa &= 1.87 \times 10^5 \text{ dyne/cm} \\ \mu &= 0.24 \times \quad \text{''} \\ \tau &= 0.20 \times \quad \text{''}\end{aligned}$$

Thus, the full line in Fig. 4 is worked out which is in comparatively good agreement with experiments, though not sufficient at the temperatures ranging from 20 to 50°K. It will be expected that the data for selenium can also be explained by a similar procedure.

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