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July 1966

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ABSTRACT

An equation of state for aluminum to the Debye approximation has been obtained from the determination of the Debye temperature, Θ, as a function of pressure from 0 to 135 kbars. The variation was determined by use of the Bloch-Grüneisen equation in fitting experimental resistance-temperature data at various pressures. The zero pressure thermodynamic properties of aluminum calculated from the equation of state agree quite well with the corresponding observed quantities. It is found that the Grüneisen ratio, $-d\ell n\Theta/d\ell nV$, is a linear function of volume at pressures above 40 kbars. An analytical expression which approximates the observed volume dependence of the Debye temperature is given by,

$$\Theta = 395\, e^{-1.78\Delta V/V_o}.$$

INTRODUCTION

Until the recent development of x-ray diffraction methods for the determination of the pressure-volume-temperature relationships of solids, nearly all of the available equation of state work on solids was at pressures above 100 kbars and was obtained using shock waves. The reliability of these measurements decreases below 100 kbars. It is certainly desirable to be able to make direct determinations from 1 atmosphere to a pressure above 100 kbars, so that there is an independent check of the shock work. It is essential that static techniques be developed for equation of state determinations so that the problem is as completely solved as possible. Recently, Bernardes and Swenson[1] have discussed the techniques and difficulties involved in the static determination of an equation of state.

Since our particular interests lie in the variation of the thermodynamic properties of a solid as a function of temperature and pressure, we are endeavoring to make determinations of the heat capacity as a function of temperature and pressure, and these results combined with a P-V determination at some temperature are then sufficient to completely characterize the equation of state of the solid over the range of variables studied. The normal methods of heat capacity measurements are not applicable when the system is under pressure. The practical reason is that the sample is such a small fraction of the total system. Direct measurements have been made on helium[2] and hydrogen[3] in the liquid helium temperature region. These measurements were made possible because the heat capacity of the container became negligible compared to that of the solids under investigation.

In the present paper, the heat capacity and thermodynamic properties of aluminum are determined to the Debye approximation. This is done by the determination of the Debye temperature of aluminum by the application of the Bloch-Grüneisen equation to the resistance-temperature measurements on aluminum. The Debye temperature of aluminum increases to 485°C at a pressure of 135 kbars. The value at 1 atm is 395°C.

THEORY

It is well known that the temperature-resistance behavior of a one electron metal is well described by the Bloch-Grüneisen equation,

$$R = C \frac{T^5}{\Theta^6} \int_0^{\Theta/T} \frac{x^5 dx}{(e^x-1)(1-e^{-x})} \qquad (1)$$

The discussion of this result can be found in any elementary text on solid state physics, for example that of Ziman.[4] In actual practice, the absolute values of the resistance are not accurately given by this equation, but the relative resistances as a function of temperature dervied from this equation are in excellent agreement with those obtained from experiment. The equation is of use in equation of state investigations because it contains as its one parameter, the Debye temperature, Θ_D. At one atmosphere, where the limitations on the temperature that is attainable is not the limiting factor in the investigation, the Debye temperature is determined from the ratios of the parameters in the regions which exhibit a linear and fifth power dependence of the resistance on temperature. The Debye temperatures determined in this manner for one electron metals agree well with the values obtained by other methods.[5] Aluminum behaves as a one electron metal at one atmosphere with respect to the application of the Bloch-Grüneisen equation. The Debye temperature obtained from the

electrical resistivity is 395°C, while other values range from 385° to 411°C. The other values come from specific heat and elastic constant determinations at different temperatures. In this paper, the assumption is made that aluminum continues to behave as a one electron metal to the highest pressure involved in this investigation, 135 kbars.

Once the Debye temperature is known as a function of pressure, the partition function can be evaluated, and the equation of state is

$$P = -\frac{dU_o}{dV} + \frac{\gamma}{V} U_D \qquad (2)$$

where U_o is the potential energy, P the pressure, V the molar volume, U_D the lattice vibrational energy and γ is $-d\ell n\, \Theta / d\ \ell n\, V$. U_D is given by the appropriate Debye integral.

To completely characterize the system it is essential to have a knowledge of P vs. V at some temperature. The volume data used in this investigation are those obtained by Bridgman[6,7] from compressibility work at room temperature and from the x-ray diffraction work of Jamieson.[8]

It is evident that once the partition function has been obtained, all of the properties of the system are characterized, and the validity of the results is limited by the degree of correctness of the partition function. The Debye theory does reproduce the experimental work with a high degree of accuracy when the temperature is high, i.e., about 0.5 Θ_o or greater. At lower temperatures the errors mount.

EXPERIMENTAL

The usual Bridgman anvil setup was used, but because of aluminum's extremely low resistivity, the standard resistance measurement technique could not be applied.[9] In the low temperature region (<100°K) the contact resistances of the system become appreciable compared to the resistance

of the sample. Thus, the four-lead technique described previously[10] was used and proved satisfactory. The experimental temperature region was 65 to 300°K. The lowest temperatures were reached by pumping on a liquid nitrogen bath. To maintain a warming rate of 0.1-0.3°/minute, heavy copper blocks surround the Bridgman anvils and back-up blocks. The temperature is measured with Cu-Constantan thermocouples calibrated at 77.4°, 194.7°, and 273.2°K. The aluminum used was 99.95% pure and obtained from American Lamotite Corporation.

Samples were made from 0.003 in. foil cut into 0.2 in. diam. circular hoops and annealed at 200°C for several hours. The room temperature resistance of these samples was ~ .020 Ω and decreased to ~ .001 Ω at 65°K. Further details of the resistance measurements have been previously described.[9] Of the many samples prepared, five were successful, giving a total of seventeen isobars in the pressure region from 25 to 135 kbars.

In the present development of the art of high pressure determinations at low temperatures, it was not possible to reach temperatures sufficiently low so that the fifth power temperature dependence of the resistance could be observed. It was therefore essential to fit the data obtained to the Bloch-Grüneisen equation. Obviously, the lower the temperature, the better the fit. It was found on the data obtained with aluminum, that if the lowest temperature reached was on the order of 0.25Θ, a fit to about 5° could be obtained. The lower the temperature reached, the more certain the assignment of the Debye temperature. At 65°K, the temperature was about 0.15Θ. The higher the pressure, the greater this fraction becomes. We feel that the assignment of ±5° is a reasonable estimate of the accuracy of the present experiments. Since the presently available static pressure-volume data on aluminum extends to 100 kbars, the equation

of state is valid only to this pressure. However, the Debye temperature determinations have been made to a pressure of 135 kbars.

CALCULATIONS

The procedure followed for the determination of the Debye Θ for each isobar follows. First, it must be pointed out that R, defined according to Eq. (1), must be at constant volume. Since all data taken here were obtained at constant pressure, a correction should be added, according to the formula,

$$(\partial R/\partial T)_V = (\partial R/\partial T)_p - R(\partial \ell nR/\partial \ell nV)_T \alpha \qquad (3)$$

where α is the thermal expansion coefficient at temperature T. It was found that this correction and also that for the residual resistance is negligible in the temperature region studied here.

The technique for choosing the best Θ for a particular isobar is a simple one. First, several Θ's are chosen at 5° intervals about an estimated Θ for the case. Then, reduced resistance curves derived from Eq. (1) are calculated choosing both a high and low temperature fixed point. The resulting tabulations are then compared with the experimental resistance and by a suitable minimization procedure the best Θ is chosen. The high and low temperature fixed points gave values for the best Θ separated by a few degrees from which an average was taken. Figure 1 illustrates a typical fit of the experimental data using a low temperature fixed point. The deviation from the base line (Θ = 435°) is plotted against temperature. The resulting P-Θ curve is shown in Fig. 2.

RESULTS AND DISCUSSION

From the P-V isotherm discussed earlier and the P-Θ curve obtained, the variation of Θ with V or the more useful quantity γ, defined as the Grüneisen ratio,

$$\gamma = -d\ell n\Theta/d\ell n\ V,$$

may be determined. The Grüneisen ratio has received a great deal of attention because of its application to equation of state and thermal expansion measurements.[11] Since the quantity γ/V or $d\ell n\ \Theta/dV$ appears in the equation of state, $\gamma/(V/V_o)$ is illustrated in Fig. 3. At zero pressure the value of $\gamma/(V/V_o)$ is 2.08. This compares favorably with the value of 2.19±.10 obtained from thermodynamic data.[12] As the volume decreases $\gamma/(V/V_o)$ decreases, approaching a constant value of approximately 1.7 above 40 kbars. Kormer et al.[13] have determined the Grüneisen ratio in shock wave experiments for aluminum from 700 kbars to several megabars. They have extrapolated their data to zero pressure using a value of 2.13 for γ obtained from atmospheric thermodynamic data. Although a direct comparison may not be made with our data, Kormer finds also that $\gamma/(V/V_o)$ is approximately constant up to 600 kbars and equal to 2.08. The value of $\gamma/(V/V_o)$ which best fits the data obtained here from 0 to 100 kbars is 1.78. The equation of state may then be approximated by the analytical expression

$$\Theta = 395\ e^{-1.78\ \Delta V/V_o}$$

The exponential dependence of the frequency on volume leads one to believe that a Morse potential might describe the total energy of the system. Slater[14] and more recently Pastine[15] have shown that a Morse potential does quite well for several cubic metals including aluminum.

Pastine obtains excellent agreement with shock wave data on aluminum, and calculates a change in the Debye temperature of 85° for a pressure of 100 kbars compared with 75° found in this work.

With the above results, the equation of state is defined. dU_o/dV is then integrated to obtain the total energy at absolute zero which is illustrated in Fig. 4, where volume has been converted to interatomic distance in the solid. The atomic separation at 0°K is then 2.850 Å. This compares with 2.851 Å obtained by extrapolation of x-ray data.[16] P-V isotherms were obtained from the equation of state and the corresponding volume-pressure derivative, $(\partial V/\partial P)_T$, has been tabulated in Table 1. From the thermodynamic identity

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_P,$$

the thermal expansion is calculated from tabulated Debye entropy functions. These results are given in Table 2, along with a comparison with experimental data at 1 atm. Similarly, $(C_p - C_v)$ is calculated and the results tabulated in Table 3. C_v is easily obtainable from tabulated Debye heat capacity functions. As mentioned above, direct measurement of heat capacities are being performed in this laboratory although the technique is not yet fully developed. Some preliminary results on aluminum at 50 kbars are shown in Fig. 5. The curve drawn through the experimental points is the heat capacity, C_p, determined from our equation of state.

From the Debye temperatures and compressibility data, Poisson's ratio, σ, has been calculated and is illustrated in Fig. 6. The initial value of σ is 0.35 and is nearly independent of pressure up to about 40 kbars, where it begins to increase slowly to a value of 0.38 at 100

kbars. This result is in agreement with elastic constant determinations up to 10 kbars,[17,18] where Poisson's ratio is found to be independent of pressure. Utilizing the elastic constant data further, Debye temperatures were calculated. The Debye temperature is found to have a somewhat greater volume dependence than observed here. The initial value of the Grüneisen ratio is 2.50, which is considerably larger than the thermal value of 2.19 and the value 2.08 determined here. Extrapolation to 100 kbars yields a Debye temperature 13% greater than observed in this work.

Lastly, the variation of ΔU, ΔH, ΔA, ΔF, and ΔS are shown in Table 4 as a function of pressure at 298°K. This essentially completes the thermodynamic data. Many more tabulations could be made, but additional information may be readily calculated from the data presented here.

The comparisons of $(\partial V/\partial T)_p$, (C_p-C_v), C_p, γ, and V (0°K) with experimental data are very encouraging. Each agrees to within a few percent, which is remarkable in light of the approximations. At this time the validity of the results may be tested only at zero pressure. Further verification awaits further results of direct measurements of the heat capacity, C_p, as a function of pressure.

CONCLUSIONS

With the experimental procedure described, we have an easily applied technique for obtaining equation of state data applicable to a number of important metals. Since the entropy changes are already known for many high pressure transitions, a good test of the method would be the determination of the entropy change across a phase boundary by finding the change in the Debye Θ. The possibility of studying a

phase transition is being considered at this time.

Since the Debye Θ for many of the true one electron metals is very low, the temperature range used in this experiment is unsuitable for study of these metals. If liquid hydrogen temperatures could be reached easily and at a reasonable cost, this technique could be used for study of the alkali metals which have been of considerable interest to many workers.

ACKNOWLEDGEMENTS

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$-\left(\partial V/\partial P\right)_T \times 10^3$ cc/kbar Table 1

P \ T	298	250	200	150	100
0	13.48	13.26	13.04	12.85	12.66
10	12.62	12.42	12.21	12.02	11.87
20	11.80	11.62	11.42	11.25	11.12
40	10.29	10.14	9.98	9.82	9.71
60	8.95	8.72	8.64	8.55	8.48
80	7.78	7.67	7.56	7.47	7.39
100	6.76	6.68	6.60	6.54	6.48

$\left(\partial V/\partial T\right)_P \times 10^5$ cc/deg Table 2

P \ T	298	250	200	150	100
0	64.1	61.0	55.9	48.8	34.4
10	54.5	53.2	49.2	42.8	29.7
20	48.7	47.0	43.6	37.7	25.8
40	40.1	38.1	35.5	30.4	20.2
60	34.0	32.3	29.9	25.1	16.5
80	29.2	28.1	25.8	21.5	13.9
100	24.3	23.5	21.3	17.6	11.3

$(C_p - C_v)$ cal/deg mole Table 3

P \ T	298	250	200	150	100
0[48]	.220	.166	.112	.064	.022
0	.224	.172	.117	.068	.023
10	.171	.138	.096	.055	.018
20	.144	.114	.080	.045	.014
40	.110	.085	.060	.033	.010
60	.091	.070	.049	.027	.008
80	.079	.062	.042	.023	.006
100	.066	.053	.035	.018	.005

Table 4 Thermodynamic Functions, 298°K cal/mole

P	ΔU	ΔH	ΔA	ΔF	ΔS*
0	0	0	0	0	- 0
10	-28	2324	14	2366	- 0.10
20	-21	4634	58	4714	- 0.24
40	74	9174	213	9314	- 0.46
60	256	13616	451	13810	- 0.64
80	493	17983	734	18221	- 0.80
100	748	22268	1025	22545	- 0.92

* cal/deg mole

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Figure Captions

Fig. 1 A typical fit of the experimental data using a low temperature fixed point. The deviations from an ideal resistance curve derived from Eq. (1) (Θ = 435°) are plotted against temperature.

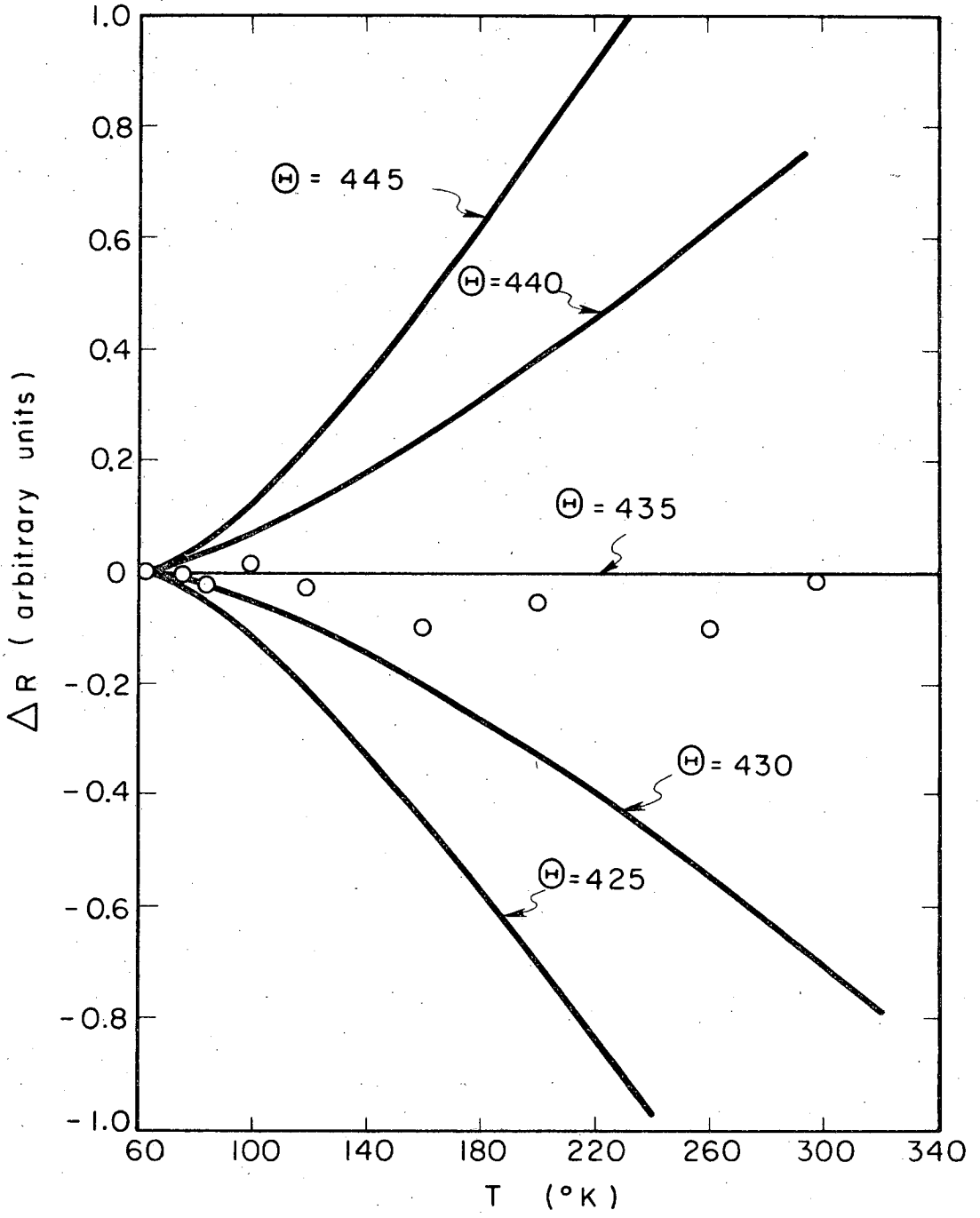
Fig. 2 Debye temperature, Θ, versus pressure for aluminum.

Fig. 3 Gruneisen ratio divided by reduced volume versus pressure and reduced volume.

Fig. 4 Total energy at 0°K versus interatomic distance.

Fig. 5 Heat capacity of aluminum at 50 kbars compared with preliminary data of Stark (unpublished data).

Fig. 6 Poisson's ratio versus pressure and reduced volume.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0.4
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0
-0.2
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ΔR (arbitrary units)
Θ = 445
Θ=440
Θ = 435
Θ = 430
Θ=425
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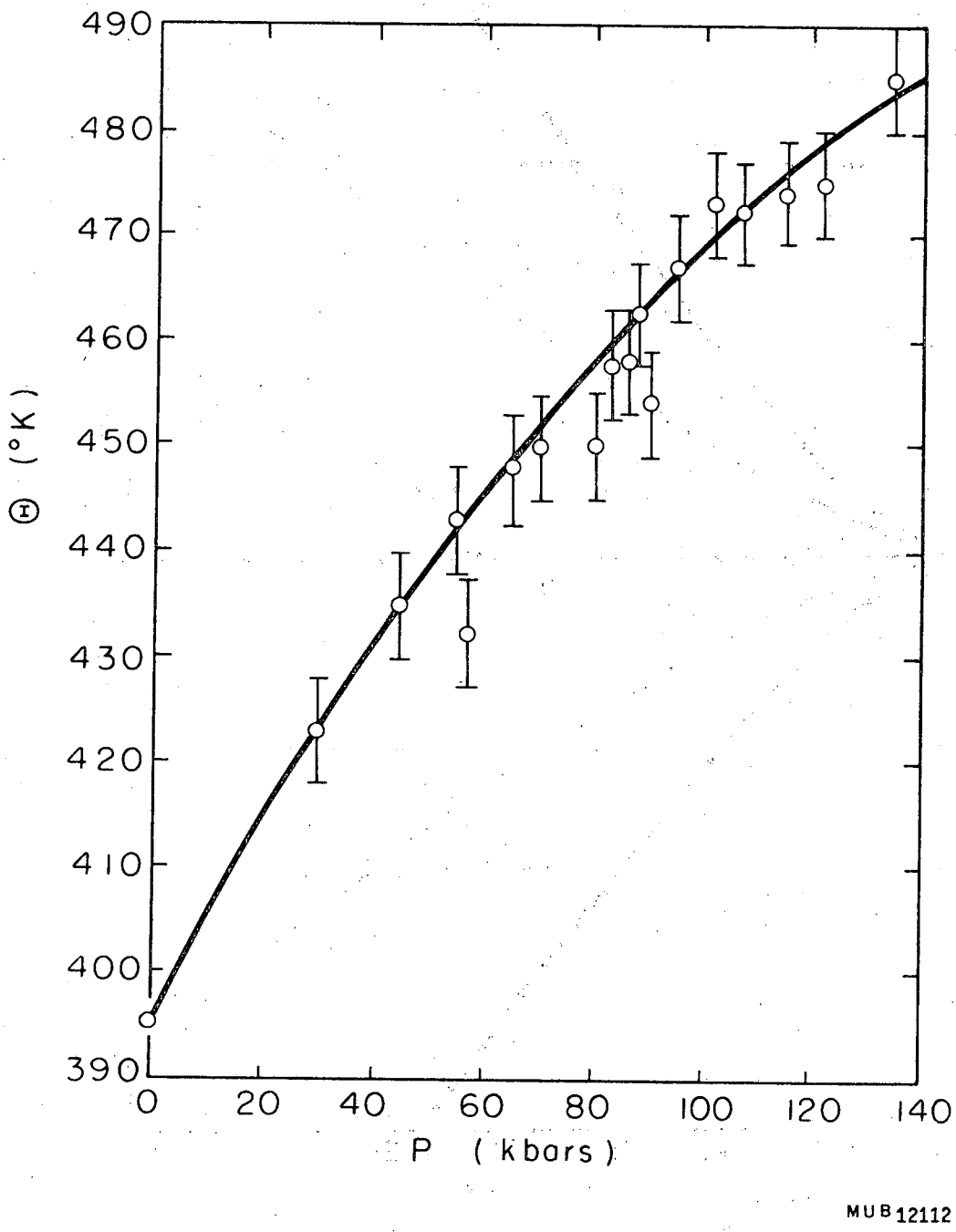
140
180
220
260
300
340
T (°K)
MUB 12111

Fig. 1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450
440
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420
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40
60
80
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120
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P (kbars)
MUB 12112

Fig. 2

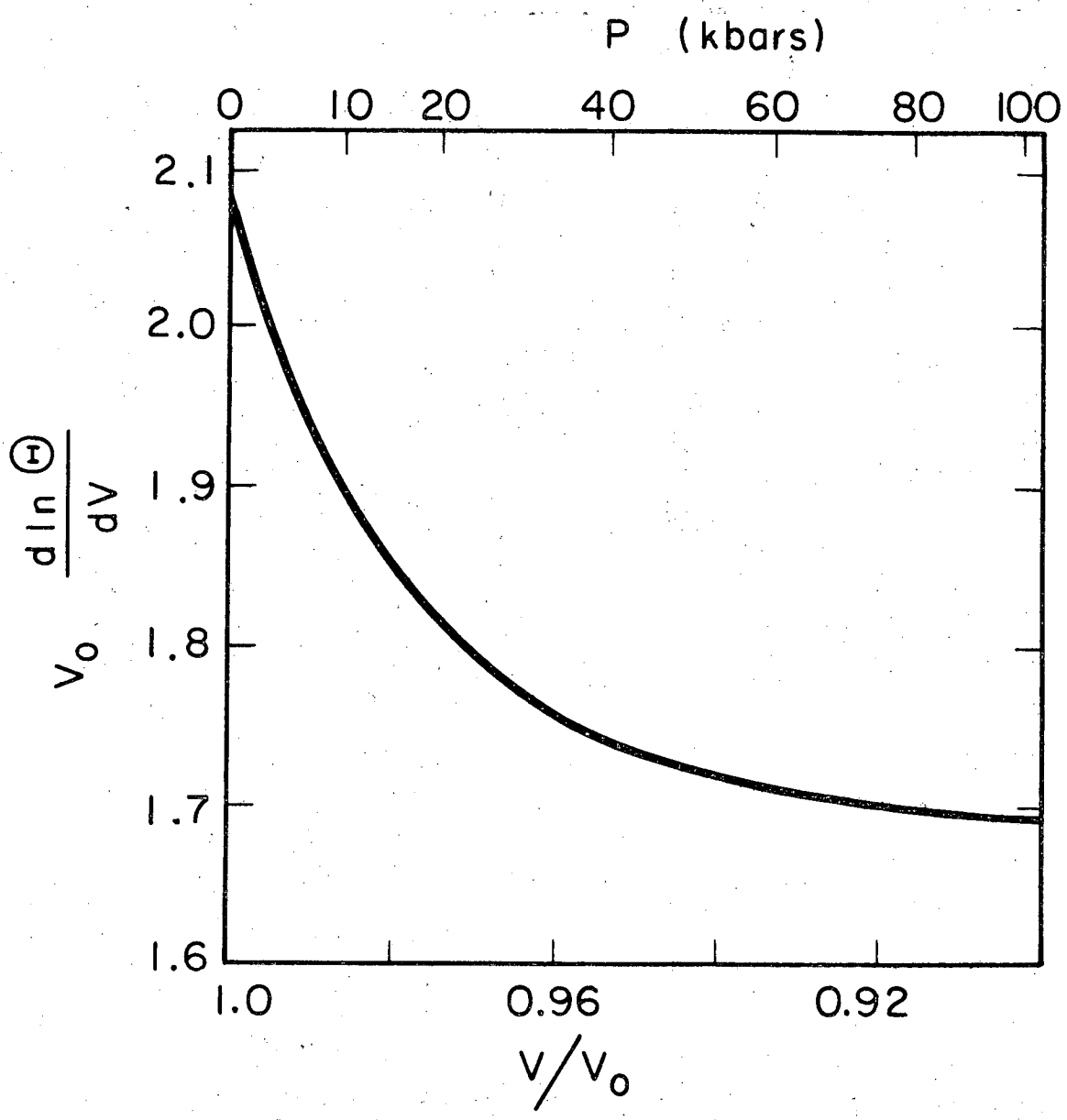

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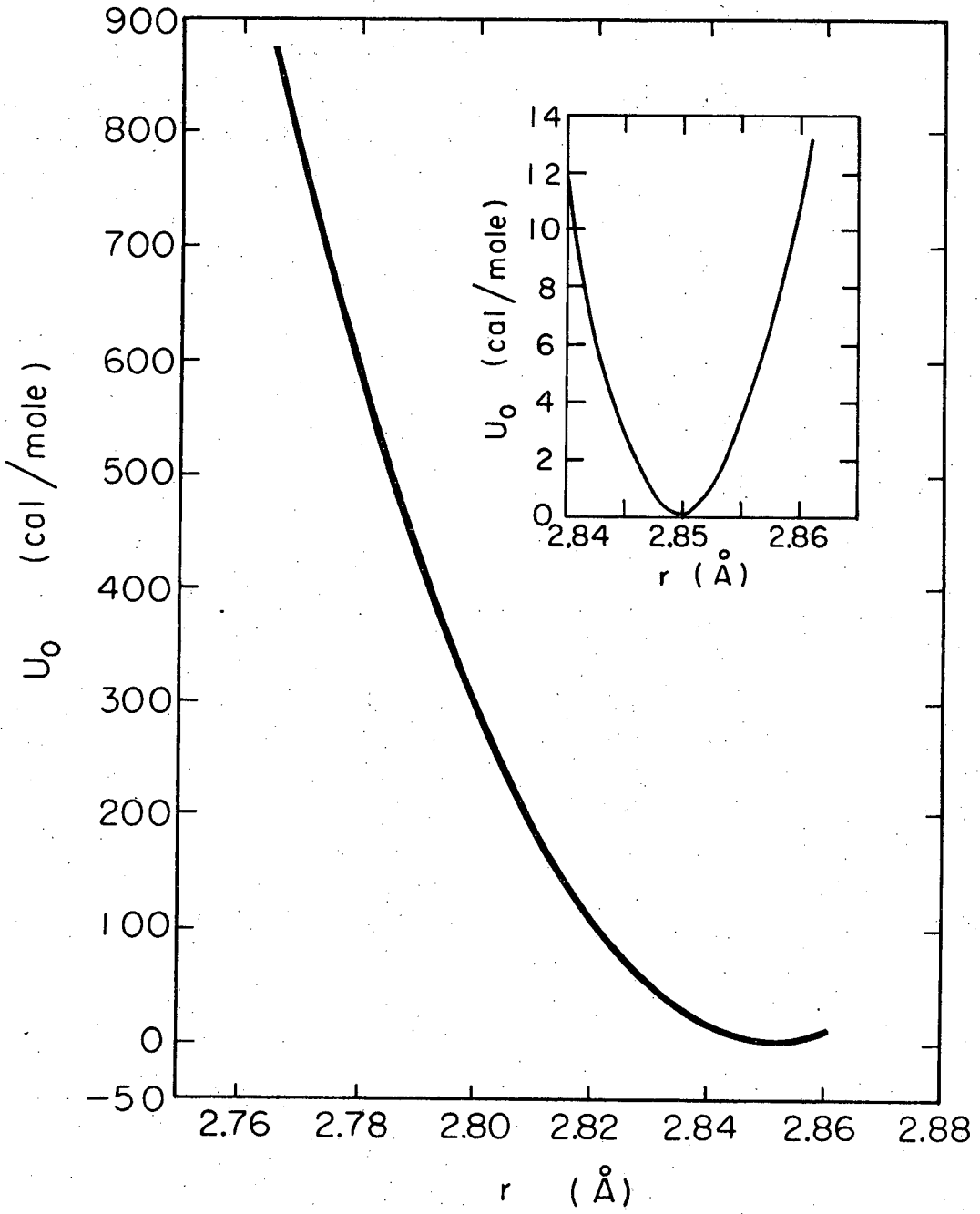
Fig. 3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2.80
2.82
2.84
2.86
2.88
r (Å)
14
12
10
8
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2.85
2.86
r (Å)
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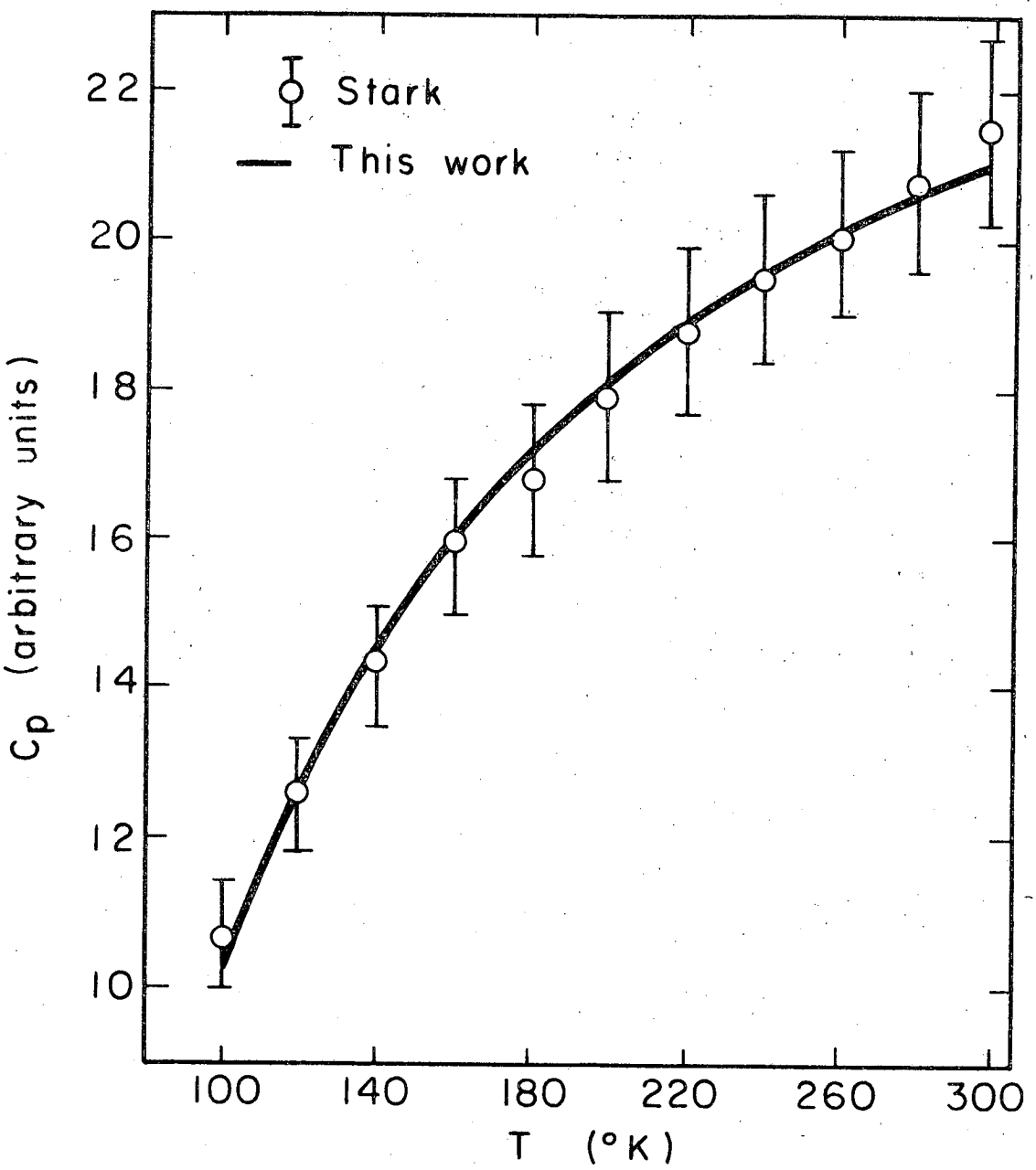
Fig. 4


Stark
This work
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180
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260
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T (°K)
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Fig. 5

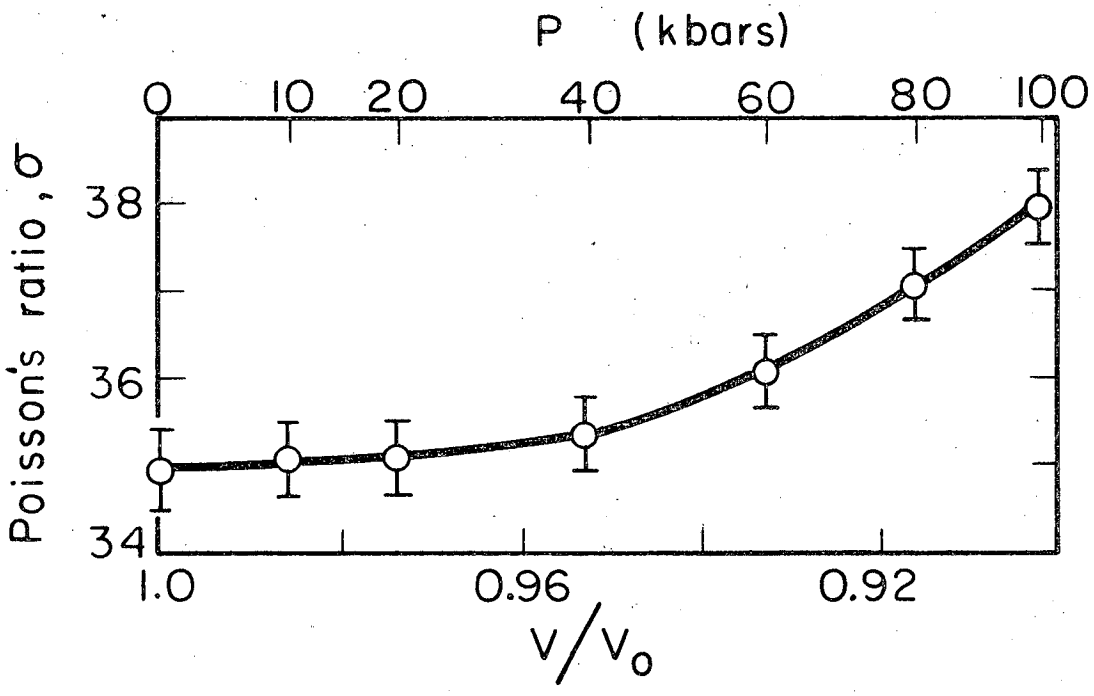

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Fig. 6

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