Thermal Conductivity and Lorenz Function of Zinc Under Pressure

P. Jacobsson[1] **and B. Sundqvist**[1]

The thermal conductivity λ and the Lorenz function L of polycrystalline zinc have been calculated from measured values of the thermal diffusivity a and the electrical resistivity ρ as functions of pressure P up to 2 GPa at room temperature. The effects of convection in, and freezing of, the pressure transmitting medium are discussed. Both λ and L increase with increasing P, with pressure coefficients of 8.7×10^{-2} and 1.5×10^{-2} GPa^{-1}, respectively. The volume dependence of L is found to be similar to that found for other simple metals. Data are also given for the Seebeck coefficient S as a function of P and for $a(T)$ and $\lambda(T)$ between 55 and 300 K.

1. INTRODUCTION

A few years ago we reported experimental data for the thermal diffusivity, a, and the electrical resistance, R, of polycrystalline zinc as functions of temperature, T, between 90 and 480 K at atmospheric pressure, and as functions of pressure, P, up to 2 GPa at 300 K [1]. We also presented corresponding data for the thermal conductivity λ, calculated from a using $\lambda = adc_p$, where d is the density and c_p is the specific heat capacity, and for the electrical resistivity ρ. We found that the resistivity data were consistent with both earlier results and simple theory and that our results for a at atmospheric pressure agreed with the TPRC [2] recommended values to within 1.5% at all temperatures.

However, when we calculated the pressure dependence of the Lorenz function, $L = \lambda\rho/T$, from the pressure dependence of λ and ρ (see Sec-

---

[1] Department of Physics, University of Umeå, S-901 87 Umeå, Sweden.

tion 3), we found a negative pressure coefficient. This was the first negative coefficient we have found for any metal [3], and it surprised us, in particular because the pressure dependence of ρ was in agreement with simple theory [4].

We decided to investigate this matter further and we soon found that the measured pressure dependence of the thermal diffusivity was in error due to various problems with the pressure transmitting medium. After identifying the problems we have tried to eliminate their contributions, as we show in Section 2. The new results are presented in Section 3 together with a brief discussion.

2. EXPERIMENTAL DETAILS

2.1. Experimental Equipment and Method

The method used is a modified Ångström method [5] capable of taking into account all lateral heat losses by conduction from the specimen to the surrounding pressure medium. Since a detailed description of the method and equipment used is published elsewhere [6], we concentrate on the details concerning the pressure medium problem.

In the modified Ångström method one end of a long rod is heated periodically with a heater voltage $U = (A + B \cos \omega_1 t + C \cos \omega_2 t)^{1/2}$ to produce a temperature wave which is the sum of two components with angular frequencies ω_1 and ω_2. The temperature wave is studied at two points on the sample with the help of thin Chromel wires spot welded to the specimen at these points and at the cold end [6]. The absolute temperatures at the first measurement point and at the cold end are measured by adding Alumel wires. With this arrangement we can find the Seebeck coefficient, S, for the specimen and also the absolute temperature at the second measurement point. Provided that the thermal diffusivity of the specimen is much larger than that of the pressure medium, it is possible to calculate the diffusivity of the specimen knowing only the distance between the thermocouples and the phase shifts and attenuations of the wave at the two angular frequencies [5]. Adding the error in the distance between thermocouples to the typical scatter, we find that the maximum error in a is about 3.5% in the high-pressure runs.

It is also possible to calculate the diffusivity, a_m, of the pressure medium simultaneously, but with a lower accuracy. This feature is used to check that the medium is hydrostatic. A glass transition or a crystallization of the medium is signaled by a large increase in the thermal diffusivity [7].

The zinc specimens, 1.1 mm in diameter and with a stated purity of 99.95%, were cut from the same wire as used previously. The wire was

obtained from Goodfellow Metals Ltd, Cambridge U.K. In order to preserve the original polycrystalline state the specimens were not heat-treated before use.

2.2. Pressure-Transmitting Media

A good pressure-transmitting medium must satisfy many conditions. Apart from the obvious ones, such as not reacting with the specimen or with the high-pressure cell, etc., we can formulate three main conditions:

First, the medium must be fluid at all pressures, because solidification leads to an unknown strain in the specimen, as shown below, and this strain results in a low measurement accuracy. In our case, the specimen is always placed horizontally in the center of the cylindrical pressure cell [6]. When changing P in a cell filled with a solid medium we get a radial mass transport, causing strain in the sample or even a change in the thermo-couple distance and thereby an underestimation of da/dP.

Second, the method is not able to take into account heat losses through convection. If convection occurs the attenuation of the heat wave increases and the thermal diffusivity will be underestimated. A medium with a high viscosity is therefore preferable.

Finally, the medium should be an electrical insulator to prevent noise signals from interfering with the thermocouple signals.

Three different pressure media, glycerol, paraffin oil, and pentane, were used in our previous experiments [1]. Glycerol is highly viscous at room temperature and does not normally solidify under increasing pressure until at the glass transition at >3 GPa [8]. When decreasing P, however, we always found that the glycerol crystallized. We illustrate this is Fig. 1: in this experiment a_m was in good agreement with literature data [7] for the liquid state at all pressures up to 1.25 GPa, for increasing P (squares, lower part of figure). After 1 night's rest at 1.25 GPa we decreased P to 1.15 GPa. The measured value for a_m was then found to be that characteristic for crystalline glycerol [7] (triangles). Each point represents the mean values of at least 10 individual measurements and the standard deviation from the mean is always smaller than the symbols.

The corresponding values simultaneously obtained for a are shown in the upper part of Fig. 1, where it is evident that glycerol is a good pressure-transmitting medium when liquid. After crystallization, however, the strain in the specimen makes accurate measurements impossible. (The apparent increase in a, when P is decreased, below 0.2 GPa is believed to originate from a reflected temperature wave which arises when the medium is partly melted).

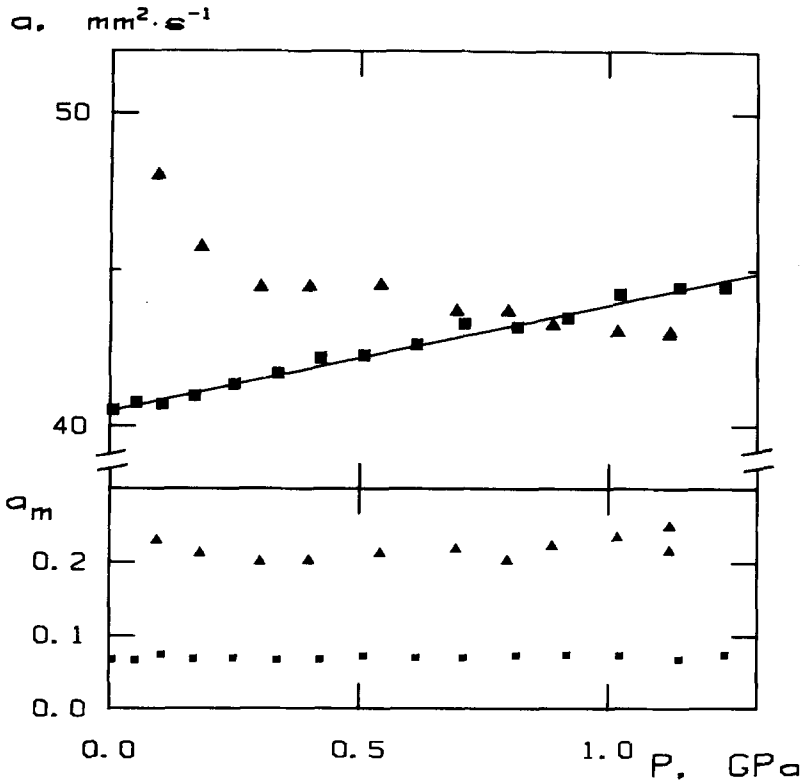After this experiment, the pressure cell was taken apart and we confir-

Fig. 1. Experimental data from one high-pressure run. Upper part: thermal diffusivity of sample; lower part, thermal diffusivity of pressure medium. (■) Increasing pressure; (▲) decreasing pressure.

med that the glycerol was in its opaque crystalline form. We then made a new experiment with the same specimen, and the data found did not differ from the straight line in Fig. 1 by more than 0.5%. It is important to point out that the results in the solid pressure medium are not reproducible, since they probably depend on the geometry of the pressure cell and on the pressure where crystallization occurred.

In our previous experiments [1] we had a leak in our pressure system which forced us to cycle up and down in pressure and to make all measurements under decreasing pressure, and those measurements were therefore probably not done under truly hydrostatic conditions. This was also the case when using paraffin oil, which solidifies at about 0.45 GPa. Pentane, on the other hand, was hydrostatic over the whole pressure range and it was therefore used as the pressure medium in most of the resistance

measurements. However, its low viscosity gave rise to large convection problems in the diffusivity measurements.

In the present experiments we have used a mixture of glycerol and ethanol, in the proportions 9:1. This mixture satisfies most of the three conditions discussed above. The high viscosity of glycerol makes convection more difficult and the addition of ethanol stops the mixture from crystallizing. The mixture was prepared under dry conditions to prevent the absorption of water, since the presence of water increases its electrical conductivity.

Before each experiment we optimized the heater signal with respect to the amplitudes and frequencies of the temperature waves. This was done in order to minimize the convection error, which is a complex function of these amplitudes and frequencies. On the one hand, using a low-amplitude signal results in a small convection error, but the scatter in the data for a is then large due to the small signals. Increasing the amplitudes decreases this scatter but also increases the risk for systematic convection errors. Changing the frequency, on the other hand, does not change the total convection current. However, at sufficiently high frequencies these currents do not follow the temperature variations, and our method is valid, but using a frequency that is too high again leads to a low accuracy due to the very large attenuation. With the glycerol–ethanol mixture we were always able to find combinations which gave a scatter of about 1 % rms and a mean value of a which did not differ from the "very low-amplitude mean value" by more than about 1%.

When the pressure was increased the convection error decreased and our only problem was then to ensure that our medium was hydrostatic.

3. RESULTS AND DISCUSSION

Three successful pressure runs were made with the glycerol–ethanol mixture as the pressure medium. At atmospheric pressure and $T = 300$ K we found $a = 0.410$ cm$^2 \cdot$ s^{-1}, from which we calculated λ to be 113 W $\cdot$ m$^{-1} \cdot$ K^{-1}. For the specific heat capacity we have used data from Eichenauer and Schulze [9] at temperatures below 292 K and from Eastman et al. [10] at higher temperatures. Our value for λ is 1 % below the value of Wilkes et al. [11] and 8 % below the TPRC [12] recommended value. As before, we note an inconsistency here: our values for a agree with the TPRC [2] values to within 1.5 % and the latter should be calculated from the λ values. We also repeated our previous measurement of $a(T)$ and $\lambda(T)$, using better low-temperature equipment which enabled us to obtain continuous data from 55 to 350 K. The new data, which are shown in the upper part of Fig. 2, were in excellent agreement with our

previous data, except that the absolute values are 2.5 % greater than those before at all T, reflecting the uncertainty in thermocouple distance. (The agreement is well within the combined experimental error.) The solid line in the figure is a fourth-order polynomial in T^{-1} fitted to the experimental data. The corresponding values for λ are shown in the lower part of Fig. 2 and it is evident that we now observe a shallow (1 %) minimum in λ at 95 K. We also show in Fig. 2 literature data from Refs. 11–13. For the data of Ref. 13 we show results for two samples, with reported purities of
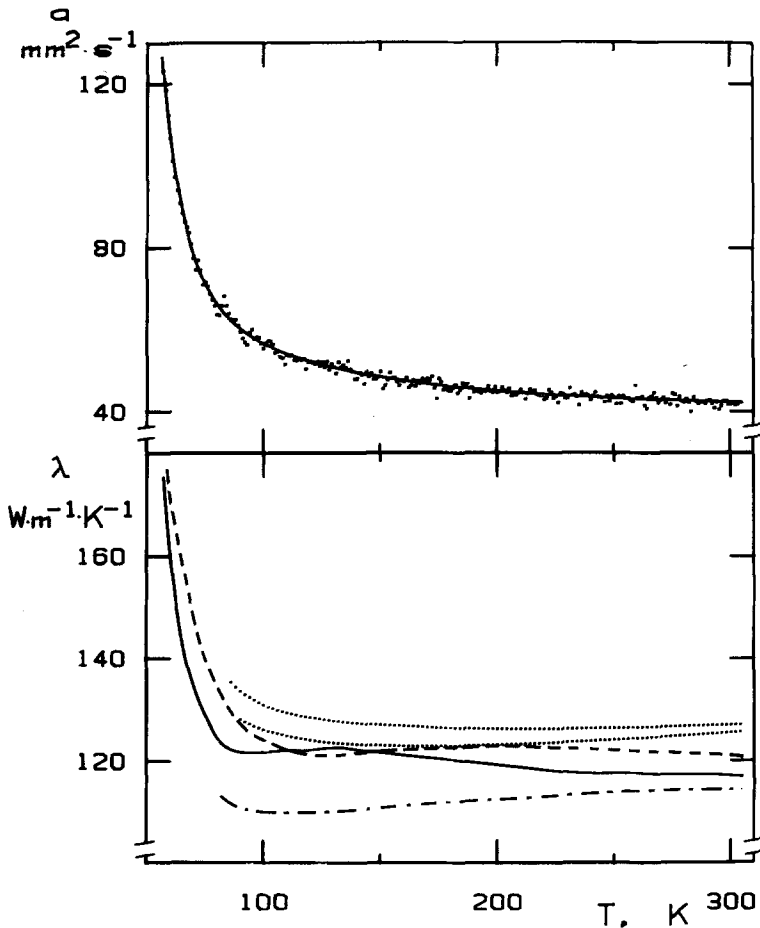

Fig. 2. Upper part: Thermal diffusivity of zinc as a function of temperature. Dots denote experimental data and the solid line is a fitted function (see text). Lower part: Thermal conductivity of zinc as a function of temperature. (−−) Our results corresponding to the fitted function; (−·−) Ref. 11; (−−) Ref. 12; (···) Ref. 13 (upper set of dots, 99.9999 % pure; lower set of dots, 99.99 % pure).

99.99 % (lower dotted line) and 99.9999 %, respectively. Apart from the fact that the data of Mucha et al. [13] show a positive $\partial\lambda/\partial T$ at all T between the minimum and 400 K, the agreement between the different sets of data is acceptable, in view of the fact that polycrystalline specimens are studied.

In Fig. 3, $a(P)$ is shown up to 2 GPa for one of our three specimens. (Again, each point represents the mean value of at least 10 individual measurements.) The three pressure coefficients $a^{-1}\partial a/\partial P$ obtained agreed well with each other, with a mean value $a^{-1}\partial a/\partial P = 7.7 \pm 0.5 \times 10^{-2}$ GPa^{-1} when corrected for the change in thermocouple distance under pressure using compressibility data from Vaidya and Kennedy [14]. The pressure dependence of λ was calculated from $\lambda = adc_p$ by using the thermodynamic identity [15],

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -\left[\alpha^2 + \left(\frac{\partial\alpha}{\partial T}\right)_P\right]T/d$$

where α is the volume expansivity. The pressure coefficient of λ was found to be $\lambda^{-1}\partial\lambda/\partial P = 8.7 \pm 0.5 \times 10^{-2}$ GPa^{-1}. This is about twice the value we obtained in the preliminary experiments [1]. It is also larger than Bridgman's results, 4.5×10^{-2} GPa^{-1} [16].

As mentioned above, the main motivation for the present work was to find a more accurate value for the pressure coefficient of L. What is
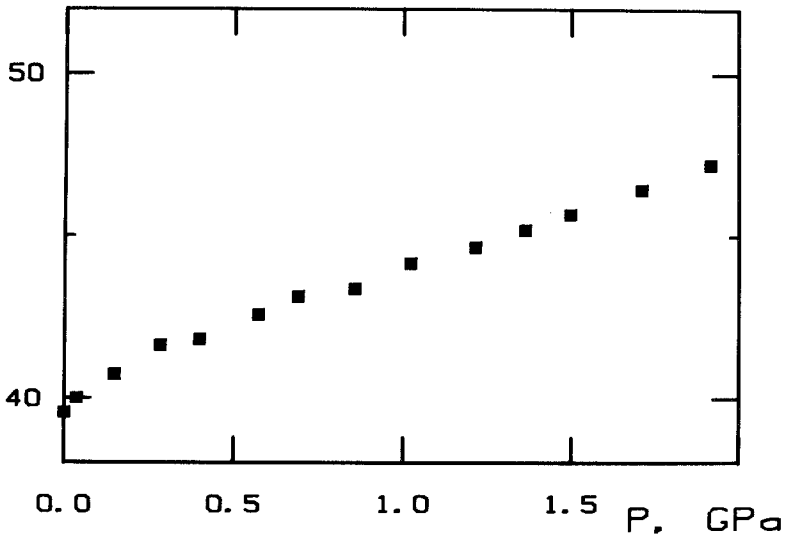

Fig. 3.   Thermal diffusivity of zinc as a function of pressure.

actually of interest is, however, the pressure coefficient of the electronic Lorenz function $L_e = \lambda_e \rho / T$, where $\lambda_e = \lambda - \lambda_g$ is the electronic thermal conductivity and λ_g the lattice thermal conductivity. In order to find the pressure coefficient of L_e we must thus first eliminate the effect of λ_g, which is about 4% of λ at 300 K [17]. There are various estimates of the pressure dependence of λ_g, but usually λ_g depends on volume as $-7\gamma < d(\ln \lambda_g)/d(\ln V) < -4\gamma$ [3, 18], where γ is the Grüneisen constant, which for zinc is 2.05 [19]. Using $d(\ln \lambda_g)/d(\ln V) = -5.5(\pm 1.5)\gamma$, we find that the pressure coefficient of λ_e is $\lambda_e^{-1}\partial \lambda_e/\partial P = 8.3 \pm 0.7 \times 10^{-2}$ GPa^{-1}, equivalent to $d(\ln \lambda_e)/d(\ln V) = -5.3 \pm 0.4$. Combining the new result for λ_e with data [1] for the pressure coefficient of the resistivity, $\rho^{-1}\partial \rho/\partial P = -6.6 \pm 0.2 \times 10^{-2}$, we find that $L_e^{-1}\partial L_e/\partial P = 1.2 \pm 0.9 \times 10^{-2}$ GPa^{-1}, not very different from the pressure coefficient $L^{-1}\partial L/\partial P = 1.5 \pm 0.7$ GPa^{-1} for the total L. The corresponding volume derivative is then $d(\ln L_e)/d(\ln V) = -0.7 \pm 0.6$. In theory, the latter quantity should be very small and positive [3], but in practice it is usually found to be between 0 and -1, at least for simple metals [3]. The present results show that this is also true for the fairly simple metal zinc.

   The Seebeck coefficient, S, was found to be 1.9 μV · K^{-1} at atmospheric pressure and 310 K, increasing by 0.52 μV · K^{-1} · GPa^{-1} (see Fig. 4). S has previously been measured for single crystals of zinc by Rowe
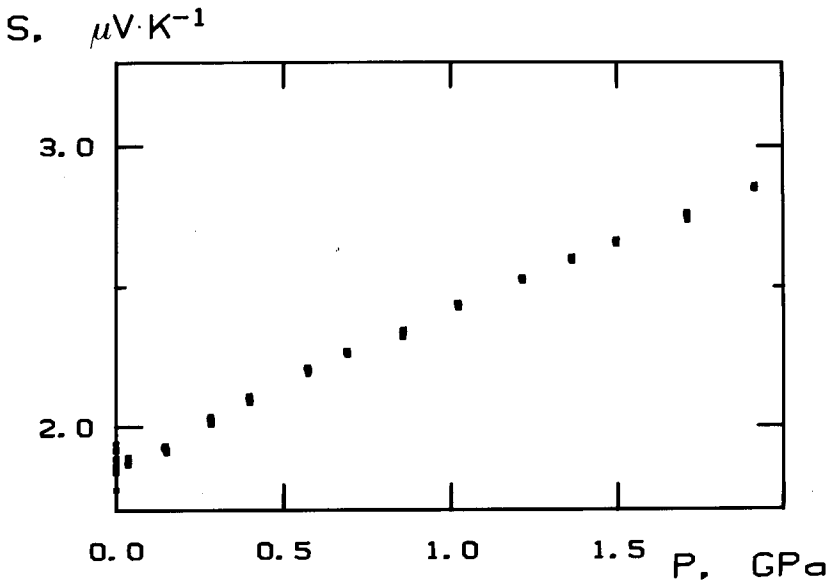

Fig. 4.   Seebeck coefficient as a function of pressure.

and Schroeder [20], who found S to be about $1\ \mu V \cdot K^{-1}$ parallel to the crystal axis and $3\ \mu V \cdot K^{-1}$ perpendicular to it at atmospheric pressure and 300 K. As expected, our value for the polycrystalline material lies between these results. The pressure dependence agrees well with the results of Bridgman [21], who found that the increase in S is about $0.6\ \mu V \cdot K^{-1} \cdot GPa^{-1}$ at room temperature.

REFERENCES

1. P. Jacobsson and B. Sundqvist, *High Temp.- High Press.* **17**:103 (1985).
2. Y. S. Touloukian, R. H. Powell, C. Y. Ho, and M. C. Nicolaou, *Thermophysical Properties of Matter, Vol. 10. Thermal Diffusivity* (IFI/Plenum, New York, 1973), pp. 216–219.
3. R. G. Ross, P. Andersson, B. Sundqvist, and G. Bäckström, *Rep. Progr. Phys.* **47**:1347 (1984); B. Sundqvist, *Mater. Res. Soc. Symp. Proc.* **22**(I):261 (1984).
4. J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960), pp. 418–420.
5. B. Sundqvist and G. Bäckström, *Rev. Sci. Instrum.* **47**:177 (1976).
6. P. Jacobsson and B. Sundqvist, *J. Phys. Chem. Solids* **49**:441 (1988).
7. O. Sandberg, P. Andersson, and G. Bäckström, *J. Phys. E* **10**:474 (1977).
8. O. Sandberg, P. Andersson, and G. Bäckström, in *Proc. 7th Symp. Thermophys. Prop.*, A. Cezairliyan, ed. (ASME, New York, 1977), pp. 181–184.
9. W. Eichenaur and M. Schulze, *Z. Naturforsch. Teil A* **14**:28 (1959).
10. E. D. Eastman, A. M. Williams, and T. F. Young, *J. Am. Chem. Soc.* **46**:1178 (1924).
11. K. E. Wilkes, R. W. Powell, and D. P. DeWitt, in *Thermal Conductivity: Proceedings of the 8th Conference*, C. Y. Ho and R. E. Taylor, eds. (Plenum, New York, 1969), pp. 3–7.
12. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysics Properties of Matter, Vol. 1. Thermal conductivity: Metallic Elements and Alloys* (Plenum, New York, 1970), pp. 453–460.
13. J. Mucha, K. Galuzewski, A. Jezowski, and J. Rafalowicz, *Phys. Stat. Sol. (b)* **142**:K57 (1987).
14. S. N. Vaidya and G. C. Kennedy, *J. Phys. Chem. Solids* **31**:2329 (1970).
15. K. P. Rodionov, *Sov. Phys.- Tech. Phys.* **11**:955 (1967).
16. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **57**:77 (1922).
17. G. K. White, in *Thermal Conductivity: Proceedings of the 8th Conference*, C. Y. Ho and R. E. Taylor, eds. (Plenum, New York, 1969), pp. 37–43.
18. G. A. Slack, *Solid State Phys.* **34**:1 (1979).
19. K. A. Gschneidner, Jr., *Solid State Phys.* **16**:276 (1964).
20. V. A. Rowe and P. A. Schroeder, *J. Phys. Chem. Solids* **31**:1 (1970).
21. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **53**:269 (1918).