

Pressure Dependence of Melting Temperature for Metals**Die Druckabhängigkeit der Schmelztemperatur von Metallen****Зависимость температуры плавления от давления для металлических элементов**

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Summary

A new theory for the melting curve of metals is proposed. The theory is based on a new equation of state for metals, called MY, on LINDEMANN's law and on the volume dependence of the GRÜNEISEN parameter after MIGAULT. In MY, the repulsive and attractive lattice terms, FERMI term, exchange and correlation terms of the electrons as well as a quantum-statistical correction have been taken into account. The geophysical motivation for this study is outlined in the first chapter.

Zusammenfassung

Es wird eine neue Schmelzpunkt-Theorie für Metalle vorgeschlagen. Die Theorie beruht auf einer neuen Zustandsgleichung für Metalle, die MY genannt wird, auf dem Lindemann-Gesetz und auf der Volumenabhängigkeit des Grüneisen-Parameters nach MIGAULT. In MY sind der abstoßende und der anziehende Gitterterm, der Fermi-Term, der Austausch- und Korrelationsterm der Elektronen sowie eine quantenstatistische Korrektur berücksichtigt. Der geophysikalische Grund für diese Untersuchung wird im Eingangskapitel dargelegt.

1. Introduction: Geophysical Motivation

At present, it is generally accepted that the geomagnetic main field is generated by a dynamo in the outer core of the earth. The multitude of possible mechanisms is limited by geophysical studies. Since the liquid outer core is surrounded by the lower mantle, the way in which the heat is dissipated outward through the latter (cf. [53, 47]) plays a certain part in view of the fact that this has a bearing on the boundary conditions of the hydromagnetic convection. Furthermore, the question arises whether convection in the outer core may be thermally driven ([17, 40, 41]). It turned out that the solution to this question depends almost exclusively on the unknown pressure dependence of the melting temperature of the metallic core of the earth. Nowadays, it is assumed that iron is the main constituent of the outer core (see, e.g., RINGWOOD [31] and others quoted there). On account of the cosmic abundances, however, minor amounts of nickel and other metals may also be expected. As the density of the outer core is lower than that of iron and the transition metals adjacent in the Periodic Table, light elements (O, S, Si, C, etc.) probably also occur in the mixture. The computed models are mostly based on a binary mixture. If one assumes, e.g., an iron-sulphur mixture, one arrives at different mixtures depending on the equations of state used and other assumptions: 15 ... 17 wt % sulphur according to USSELMAN [42], 9 ... 12 wt % according to AHRENS [1] and 5 ... 10 wt % according to BROWN and McQUEEN [8]. Even under zero pressure, it is difficult to determine the phase diagram Fe—S (RAU [30]). KUBASCHEWSKI [20] gives a review of the multitude of binary phase diagrams of iron at normal pressure. BEKE et al. [6] show how the phase diagram of binary metal alloys is computed. Now, when realistically considering the problem of the melting temperature of the outer core, one has to be aware of the following aspects:

- a) The assumption that the outer core is composed of just two elements is only a convenient fiction. Other metals, too, and more than one light element are certainly involved. Due to the complex packings of atoms, even minor additions may significantly modify the melting temperature, usually making it lower.
- b) Various approaches exist nowadays for the computation of the melting temperature of just one phase of an element in the case of high pressures, all of these approaches being partly empirical.
- c) In particular in respect of iron, the situation is made more complicated by the occurrence of various phases. At (200 ± 2) GPa and (250 ± 10) GPa, the elastic wave velocities as a function of pressure along the Hugoniot of iron exhibit jumps whose identification with the well-known phases of iron still poses some difficulties [7]. This question is relevant inasmuch as the jumps are occurring in the pressure range of the earth's outer core.
- d) Even if the material mixture were known and, what is more, even if it would be a well-known binary mixture and the melting-temperature density curve of the individual components would be computable, it would still not be possible to directly compute the phase diagram for high pressures from the zero-pressure phase diagram, since sudden changes in the atom packings may still occur in between.

This paper is designed to make a contribution to the partial problem b) only and to suggest a more realistic way of computing the melting temperature of pure metals as a function of pressure. The results are to be verified with the aid of measured values.

2. Physical Preliminaries

Melting is a complex phenomenon. Obviously, there are two basically different kinds of melting processes: quantum melting [18] occurring in superconductors and melting due to thermal effects. We are going to consider only the latter case. The great variety of chemical bonding structures results in a multitude of thermal mechanisms for the transition from the crystalline to the liquid state. For a small number of semi-metallic materials, the volume change on melting $\Delta V_m/V_s$ is negative. With these materials, e.g., Ga, Bi and Sb, the melting temperature T_m decreases with the pressure p . They also include the semi-conductors Si and Ge whose behaviour follows from their covalent bonding (VAN VECHTEN [44], SOMA and MATSUO [35]). With almost all metals, $\Delta V_m/V_s$ is positive and, due to the CLAUSIUS-CLAPEYRON equation, the melting temperature increases with the pressure until phase changes are initiated. Prior to the phase change, the melting curve will decrease a little and rise again thereafter. The phase changes of the metals are caused by the rearrangement of the atoms to more close-packed lattices or by electron shell collapse. We shall, however, only consider the melting curves of the metals within *one* phase. BORN's original suggestion that the entire lattice becomes unstable during melting apparently is not correct (COTTERILL and MADSEN [11]). Instead, in the course of heating, more and more dipole pairs of dislocations are formed (KUHLMANN-WILSDORF [21]) which, when reaching a certain concentration, destroy the cohesion of the lattice structure and lead to a mutual dislocatability of the lattice fragments, i.e., macroscopically to fluidity (NINOMIYA [29]). The free volume theory is an alternative description of the same phenomenon (GÓRECKI [14]). The LINDEMANN melting hypothesis is compatible with the dislocation theory and has actually often been used (cf. [33, 22, 36]). The author [49] derived a formula for the pressure dependence of the melting temperature from a dislocation model and an interatomic LJ potential. He proved that the same formula can also be derived from the equation of state by ULLMANN and PAN'KOV [39], the formula by VASHCHENKO and ZUBAREV [45] for the volume dependence of the GRÜNEISEN ratio and from LINDEMANN's melting law. Agreement

Table 1

Material parameters of the metals used. Z is the atomic charge, w the valency. The parameter j is given after MIGAULT et al. [25], the atomic value v_0 after GÓRECKI [14], the melting temperature T_{m_0} at vanishing pressure after GSCHNEIDNER [15], κ_0 and κ_1 after ULLMANN and PAN'KOV [39]. The original sources of the last two parameters are listed in the last column

Material	Z	j	v_0 (10^{-30} m ³)	w	T_{m_0} (K)	κ_0 (100 MPa)	κ_1	Reference
Mg	12	0.43	23.27	2	923	344.2	4.16	[4]
Al	13	-0.24	16.60	3	933.2	729.1	4.7	[37; 2]
Ni	28	0.67	10.94	2	1,726	1,790	6.20	[16]
Cu	29	1	11.81	2	1,356	1,330	5.65	[5]
Ag	47	0.71	17.06	1	1,234.0	1,015	5.53	[12; 43]
Cd	48	1.3	21.58	2	594.18	457.9	6.77	[4]
Pt	78	-1.2	15.10	2	2,042	2,770	5.18	[16]
Au	79	-0.92	16.96	1	1,336.2	1,664	6.51	[5]
Pb	82	-0.75	30.33	2	600.576	419	5.72	[26]

with the measured values is not bad, but could be further improved. A large portion of the results given in a graphical form is presented in [46]. The formulas printed there are partly distorted by misprints. The correct formulas can be found in [49]. Meanwhile, the author has derived three new equations of state, a preliminary model X [48], a model Y [50] for metals yielding excellent agreement for experimental high-compression data, and a simplification of MY designated MZ [51]. The ultrasonic, static and shock-wave compression data of oxides and halides are approximated very well by the MZ curves. It should be pointed out here that much more experimental data were used for the verification of MY than in [52]. In the following, it will be attempted to arrive at a new melting theory for metals from MY, the LINDEMANN relation and the volume dependence of the GRÜNEISEN ratio by MIGAULT [23, 24]. The formula by MIGAULT is a generalization of the relation given by VASHCHENKO and ZUBAREV [45].

3. Melting Point Theory and Comparison with Experimental Data

The equation of state MY [50, 51] used here is as follows:

$$p = f_0 \left\{ \frac{2}{3} na \left[\frac{A}{x^{2n/3+1}} - \frac{B}{x^{n/3+1}} \right] + \frac{1}{3} b \cdot r_{s0}^3 \left[\frac{2 \cdot C}{y^{5/3}} - \frac{D}{y^{4/3}} - \frac{E}{(y^{1/3} + F)^2 y^{2/3}} \right] \right\} \quad (1)$$

where p is the pressure and x the zero-pressure density to density ratio. The following substitution holds:

$$y^{1/3} = r_{s0} \cdot x^{1/3}. \quad (2)$$

The mean interelectronic spacing at vanishing pressure is expressed in BOHR units and is computed as follows:

$$r_{s0} = [3v_0/(4\pi w a_1^3)]^{1/3} \quad (3)$$

where v_0 is the atomic volume in 10^{-30} m³ units, w is the valency of the metal, a_1 is the first BOHR radius for hydrogen. We employ $a_1 = 0.529 \cdot 17,706 \times 10^{-10}$ m. The quantities $A \dots F$ are given constants:

$$\begin{aligned} A &= 1.011, 0, & B &= 1.204, 5, \\ C &= 2.21 \text{ Ryd} \cdot (\text{Bohr unit})^2, & D &= 0.916 \text{ Ryd} \cdot \text{Bohr unit}, \\ E &= 0.88 \text{ Ryd} \cdot \text{Bohr unit}, & F &= 7.8 \text{ Bohr unit}. \end{aligned} \quad (4)$$

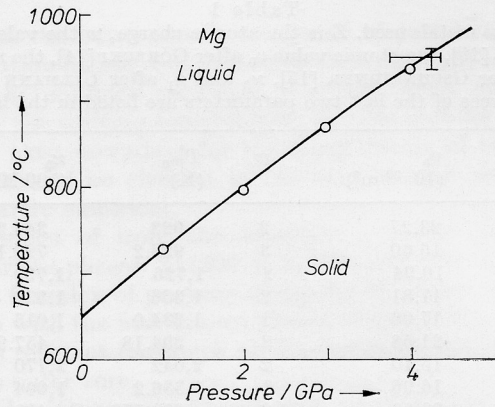


Fig. 1. Melting curve for magnesium. Experimental data after [19]

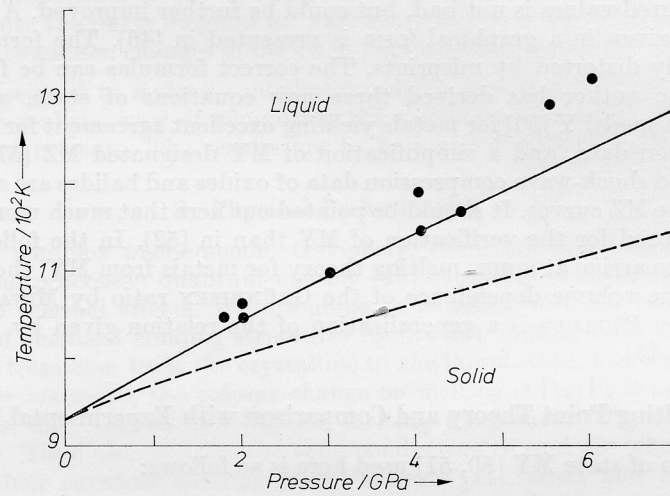


Fig. 2. Melting curve for aluminum. Experimental points after [32]. The dashed curve, however, is obtained by means of the formula by VASHCHENKO and ZUBAREV [45]

f_0 is computed from the atomic charge Z :

$$f_0 = \frac{0.72Z^{7/3} - 0.24Z^2 + 0.43Z^{5/3}}{0.768,9Z^{7/3}}. \quad (5)$$

The material constants a , b , and n are functions of the initial bulk modulus κ_0 and the initial pressure derivative of the bulk modulus κ_1 . Their substitution by κ_0 and κ_1 is effected by using

$$\left(-x \frac{\partial p}{\partial x}\right)_{x=1} = \kappa_0 \quad \text{and} \quad \left(-x \frac{\partial \kappa}{\partial x}\right)_{x=1} = \kappa_0 \kappa_1. \quad (6)$$

As a result, the equation of state MY has five material dependent input parameters, namely κ_0 , κ_1 , w , v_0 , Z . It is well adapted to the physics of metals: The terms on the right-hand side of (1) signify in that order repulsive and attractive lattice term, FERMI term, exchange and correlation term of the electrons. f_0 is a quantum-statistical correction (cf. [50, 51]). Since MY is a good approximation of the metal compression

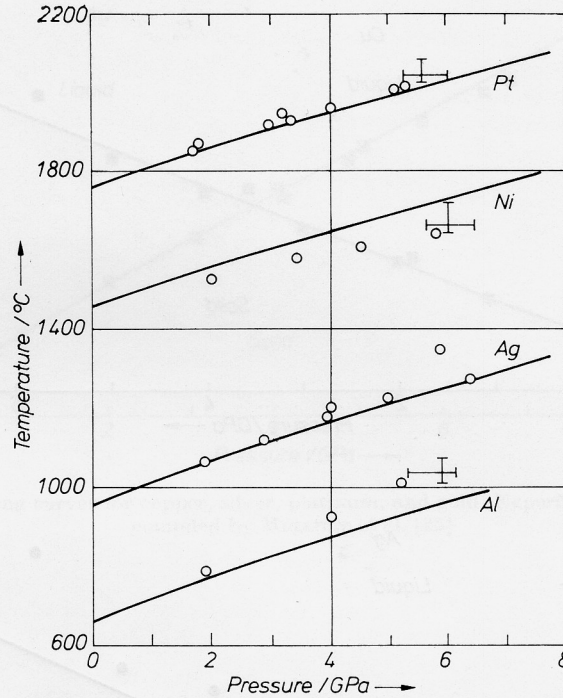


Fig. 3. Melting curves for platinum, nickel, silver, and aluminum. The experimental data have been compiled by GÓRECKI [14]

found experimentally [50], this equation of state obviously can also be used for computing the melting curve of metals.

LINDEMANN'S law is

$$T_m = C^* x^{2/3} \Theta_D^2 \tag{7}$$

and for the GRÜNEISEN parameter γ we have

$$\gamma = - \frac{d \ln \Theta_D}{d \ln x} \tag{8}$$

where Θ_D is the DEBYE temperature and C^* a material dependent constant. From this, we obtain

$$\frac{d \ln T_m}{d \ln x} = \frac{2}{3} - 2\gamma(x) \tag{9}$$

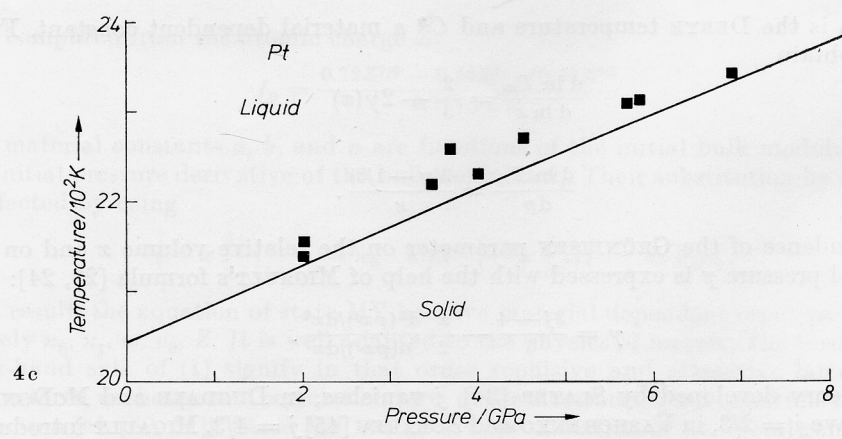
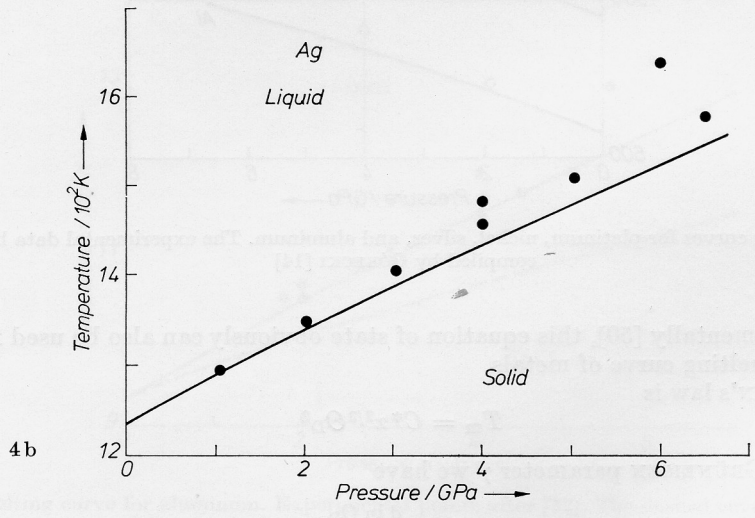
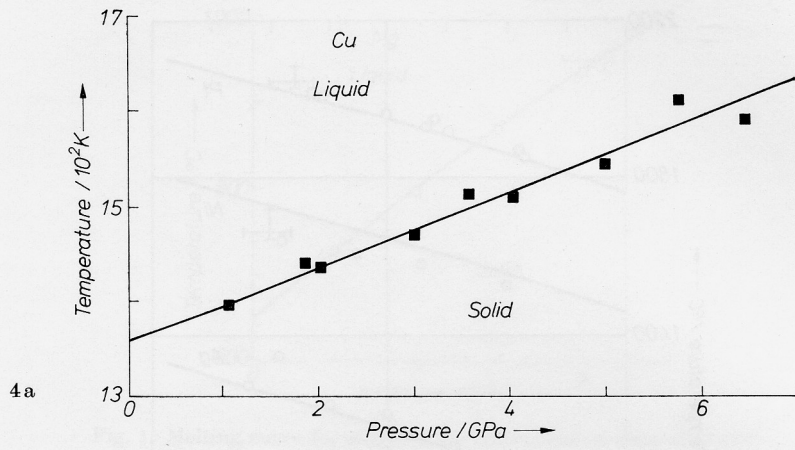
and

$$\frac{d \ln T_m}{d p} = \frac{2(\gamma - 1/3)}{\alpha} \tag{10}$$

The dependence of the GRÜNEISEN parameter on the relative volume x and on the isothermal pressure p is expressed with the help of MIGAULT'S formula [23, 24]:

$$\gamma = \frac{3j - 4}{6} - \frac{x}{2} \frac{d^2 (px^j)/dx^2}{d(px^j)/dx} \tag{11}$$

In the theory developed by SLATER [34], j vanishes, in DUGDALE and McDONALD [13] we have $j = 2/3$, in VASHCHENKO and ZUBAREV [45] $j = 4/3$. MIGAULT introduced



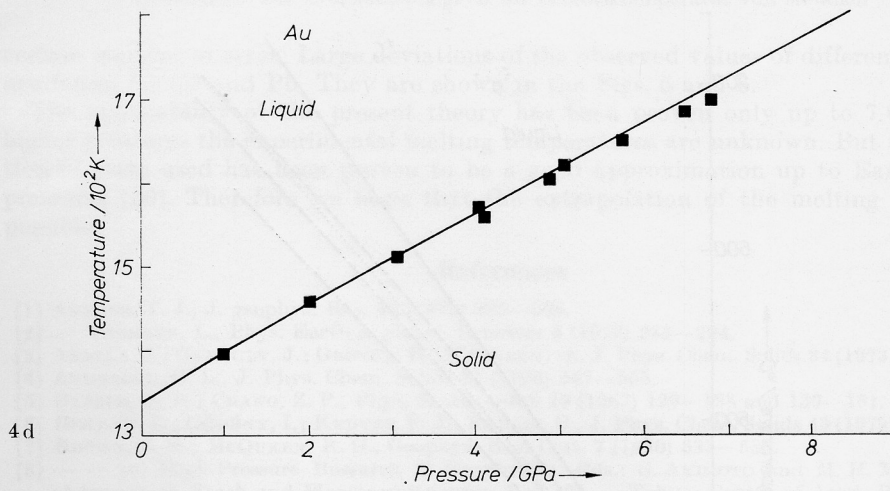


Fig. 4. a) ... d) Melting curves for copper, silver, platinum, and gold. Experimental data have been compiled by MIGAULT et al. [25]

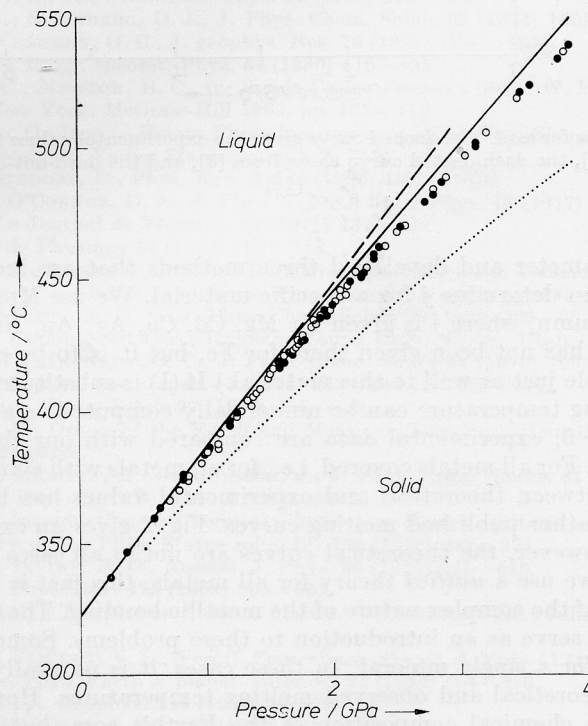


Fig. 5. Melting curves for cadmium. Experimental data after [9] (dashed curve), [19] (dotted curve), [38], [10]

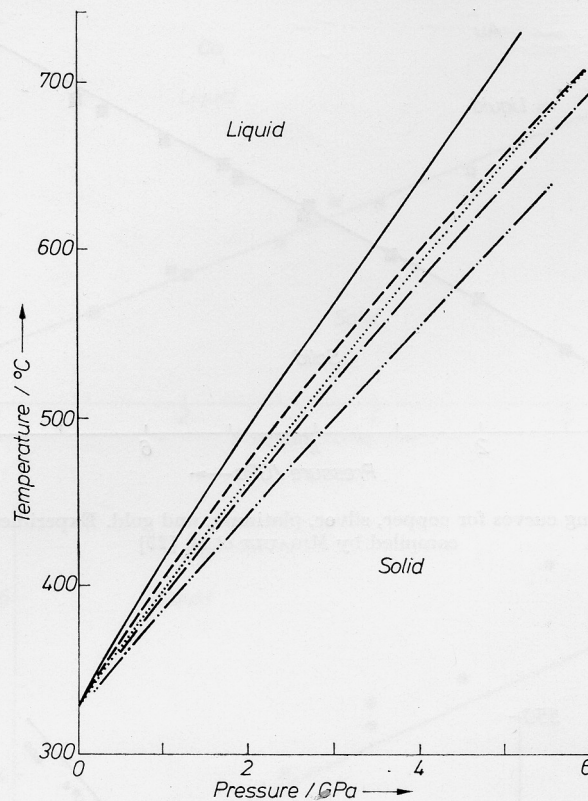


Fig. 6. Melting curves for lead. The dashed curve gives the experimental values from [28], the dotted curve those from [27], the dash-dotted curve those from [3], and the dash-dot-dot curve those from [19]

j as a scalar parameter and developed three methods that are independent of one another in order to determine j for a specific material. We use MIGAULT's et al. [25] Table 1, third column, where j is given for Mg, Cd, Cu, Ag, Au, Ni, Pt, Al and Pb. (Unfortunately, j has not been given there for Fe, but it is to be expected that the theory is applicable just as well to this material.) If (1) is substituted in (11) and (11) in (10), the melting temperature can be numerically computed as a function of pressure. In Figs. 1 ... 6, experimental data are compared with our theory represented by the solid curve. For all metals covered, i.e., for all metals with a known parameter j , the agreement between theoretical and experimental values has been improved in comparison with other published melting curves. Fig. 2 gives an example of such an improvement. However, the theoretical curves are not in all cases like least-squares fit curves. Since we use a *unified* theory for all metals, this fact is not surprising. It is a consequence of the complex nature of the metallic bonding. The references quoted in Section 2 may serve as an introduction to these problems. Some authors derived melting theories for a single mineral. In these cases, it is naturally easier to find a coincidence of theoretical and observed melting temperatures. However, we do not know exactly the chemical composition of the Earth's core, but we know that it has a metallic constitution. That is why we should search for a *unified* melting theory for metals. On the other hand, the measured values themselves apply only within

certain margins of error: Large deviations of the observed values of different authors are found for Cd and Pb. They are shown in the Figs. 5 and 6.

The applicability of the present theory has been proven only up to 7 GPa. For higher pressures the experimental melting temperatures are unknown. But the equation of state used has been proven to be a good approximation up to Earth's core pressures [50]. Therefore we hope that the extrapolation of the melting curves is possible.

References

- [1] AHRENS, T. J., *J. geophys. Res.* **84** (1979) 985—998.
- [2] — THOMSEN, L., *Phys. Earth & planet. Interiors* **5** (1972) 282—294.
- [3] AKELLA, J.; GANGULY, J.; GROVER, R.; KENNEDY, G., *J. Phys. Chem. Solids* **34** (1973) 631—636.
- [4] ANDERSON, O. L., *J. Phys. Chem. Solids* **27** (1966) 547—565.
- [5] BARSCH, G. R.; CHANG, Z. P., *Phys. Status solidi* **19** (1967) 129—138 and 139—151.
- [6] BEKE, D. L.; GÖDÉNY, I.; KEDVES, F. J.; ERDÉLI, G., *J. Phys. Chem. Solids* **40** (1979) 543—555.
- [7] BROWN, J. M.; MCQUEEN, R. G., *Geophys. Res. Lett.* **7** (1980) 533—536.
- [8] — — in: *High-Pressure Research in Geophysics*. Eds.: S. AKIMOTO and M. H. MANGHNANI (*Advances in Earth and Planetary Sciences*, Vol. 12). — Tokyo: Center of Acad. Publications 1982, pp. 611—623.
- [9] BUTUZOV, V. P.; PONYATOVSKII, E. G.; SHAKHOVSKII, G. P., *Engl. Transl. of Dokl. Akad. Nauk USSR* **109** (1956) 519—520.
- [10] CANNON, J. F., *J. Phys. Chem. Ref. Data* **3** (1974) 781—824.
- [11] COTTERILL, R. M. J.; MADSEN, J. U., *Nature* **288** (1980) No. 5790, 467—469.
- [12] DANIELS, W. B.; SMITH, C. S., *Phys. Rev.* **111** (1958) 713—721.
- [13] DUGDALE, J. S.; McDONALD, D. K. C., *Phys. Rev.* **89** (1953) 832—834.
- [14] GÓRECKI, T., *High Temp. & high Press.* **11** (1979) 683—692.
- [15] GSCHNEIDER, K. A., Jr., *Solid State Phys.* **16** (1964) 275—426.
- [16] GUINAN, M. W.; STEINBERG, D. J., *J. Phys. Chem. Solids* **35** (1974) 1501—1512.
- [17] HIGGINS, G.; KENNEDY, G. C., *J. geophys. Res.* **76** (1971) 1870—1878.
- [18] KAWAMURA, H., *Progr. theoret. Phys.* **64** (1980) 419—435.
- [19] KENNEDY, G. C.; NEWTON, R. C., in: *Solids Under Pressure*. Eds.: W. PAUL and D. M. WARSCHAUER. — New York: McGraw-Hill 1963, pp. 163—178.
- [20] KUBASCHEWSKI, O.: *Iron — Binary Phase Diagrams*. — Berlin/Heidelberg/New York: Springer-Verlag and Düsseldorf: Verlag Stahleisen m.b.H. 1982, 188 pages.
- [21] KUHLMANN-WILSDORF, D., *Phys. Rev. A* **140** (1965) 1599—1610.
- [22] MARTIN, C. J.; O'CONNOR, D. A., *J. Phys. C: Solid State Phys.* **10** (1977) 3521—3526.
- [23] MIGAULT, A., *Le Journal de Physique* **32** (1971) 437—445.
- [24] — *Le Journal de Physique* **33** (1972) 707—713.
- [25] — ROMAIN, J. P.; JACQUESSON, J., in: *High Pressure Science and Technology*. Eds.: B. VODAR and Ph. MARTEAU. — Oxford/New York: Pergamon Press 1980, pp. 938—944.
- [26] MILLER, R. A.; SCHUELE, D. E., *J. Phys. Chem. Solids* **30** (1969) 589—600.
- [27] MILLET, L. E., Unpublished Diss., Brigham Young Univ., Provo, Utah, 1968, 92 pages.
- [28] MIRWALD, P. W.; KENNEDY, G. C., *J. Phys. Chem. Solids* **37** (1976) 795—797.
- [29] NINOMIYA, T., *J. phys. Soc. Japan* **44** (1978) 263—268 and 269—271.
- [30] RAU, H., *J. Phys. Chem. Solids* **37** (1976) 425—429.
- [31] RINGWOOD, A. E.: *Origin of the Earth and Moon*. — New York/Heidelberg/Berlin: Springer-Verlag 1979, 294 pages.
- [32] ROMAIN, J. P.; MIGAULT, A.; JACQUESSON, J., *J. Phys. Chem. Solids* **41** (1980) 323—326.
- [33] SHAPIRO, J. N., *Phys. Rev. B* **1** (1970) 3981—3989.
- [34] SLATER, J. C.: *Introduction to Chemical Physics*. — New York/London: McGraw-Hill 1939.
- [35] SOMA, T.; MATSUO, H., *Phys. Status solidi (b)* **109** (1982) 387—391.
- [36] STACEY, F. D.; IRVINE, R. D., *Austral. J. Phys.* **30** (1977) 641—646.
- [37] THOMAS, J. F., *Phys. Rev.* **175** (1968) 955—962.
- [38] UBBELOHDE, A. R.: *The Molten State of Matter*. — Chichester etc.: John Wiley & Sons 1978, 455 pages.
- [39] ULLMANN, W.; PAN'KOV, V. L., *Veröff. Zentralinst. Physik d. Erde* **41** (1976) 1—201.
- [40] — WALZER, U., *Phys. Earth & planet. Interiors* **22** (1980) 204—210.
- [41] — — *Pure & appl. Geophys.* **119** (1981) 59—79.
- [42] USSELMAN, T. M., *Amer. J. Sci.* **257** (1975) 291—303.
- [43] VAIDYA, S. N.; KENNEDY, G. C., *J. Phys. Chem. Solids* **31** (1970) 2329—2345.
- [44] VAN VECHTEN, J. A., *Phys. Rev. B* **7** (1973) 1479—1507.
- [45] VASHCHENKO, V. YA.; ZUBAREV, V. N., *Sov. Phys. solid State* **5** (1963) 653—655.
- [46] WALZER, U., *Annali di Geofisica* **33** (1980) 5—36.

- [47] — Veröff. Zentralinst. Physik d. Erde **75** (1981) 1—256.
[48] — Phys. Earth & planet. Interiors **30** (1982) 62—83.
[49] — Exper. Technik Physik **31** (1983) 33—51.
[50] — A new high pressure equation of state for metals. High Temp. & high Press (in press).
[51] — Gerlands Beitr. Geophysik **93** (1984) 37—52.
[52] — ULLMANN, W.; PAN'KOV, V. L., Phys. Earth & planet. Interiors **18** (1979) 1—12.
[53] — MAAZ, R., in: Expanding Earth Symp., Sydney 1981, Proc. 1983, pp. 329—340.

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