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Pressure Dependence of the Melting Temperature of Solids

By

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Introduction A variety of theoretical expressions for the pressure dependence of the melting temperature of solids have been discussed in the literature [1 to 11]. We recently [12] presented a new expression which accurately represents the experimental melting temperature data for Ag, Cu, Au, Pt, Na, K, Rb, and Cs over a larger pressure range than the theoretical expressions previously reported in the literature.[2]) Subsequently, we demonstrated that the melting data for the rare-gas solids Ne, Ar, Kr, and Xe is accurately represented by this equation [13]. It is now of interest to test if the melting expression is applicable to partially ionically bonded solids. Recently [14], we showed that in order to accurately characterize the volume dependence of the cohesive energy of partially ionic solids, over a large range of separations, one must explicitly take into account the Coulomb contribution to the cohesive energy. Hence, it is not at all obvious that the melting expression should be valid for partially ionic solids since it is implicitly based on a covalent description of bonding.

Pressure and volume dependence of the melting point Combining Lindemann's melting temperature law, the Debye model of a solid, with the empirical observation that to a good approximation the Grüneisen parameter, γ, is directly proportional to the volume V, one obtains the following relationship [12] for the volume dependence of the reduced melting temperature:

$$T' = \exp(2\gamma_0 \Delta V/V_0)\,. \tag{1}$$

In (1) the reduced melting temperature $T' \equiv (T_m/T_{m0}X^2)$, T_{m0} is the zero pressure melting temperature, $X \equiv (V/V_0)^{1/3}$, $\Delta V \equiv V - V_0$, γ_0 is the Grüneisen parameter at T_{m0}, and V_0 is the volume at zero pressure. An equation for the pressure dependence of the melting temperature [12] is obtained from (1) by eliminating $\Delta V/V_0$ with the two-parameter analytic expression [15][3])

$$\Delta V/V_0 = \ln(1 + \beta P)/\alpha\,, \tag{2}$$

where $\alpha \equiv \beta B_0$, B_0 is the the isothermal bulk modulus at T_{m0}, and β is a fitting parameter. Substituting (2) into (1) and taking the logarithm of both sides of the equation one obtains the reduced melting equation,

$$\ln T' = \Gamma \ln P'\,, \tag{3}$$

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[2]) At low pressures our new melting temperature expression reduces to the Simon equation [1] and to several other of the previously reported expressions.

[3]) In this note we demonstrated that (2) fits the experimental compression data for twenty four different materials, to within a few percent, over the entire experimentally attainable pressure range.

Table 1
Extrapolated bulk modulus values

	T_r (K)	B_0 (10^8 Pa)	T_{m0} (K)	B_0 (10^8 Pa)
NaCl	773	157.3	1073.6	108.60
AgCl	300	417.0	729.6	315.07
AgBr	300	364.0	705.0	275

where the reduced pressure variable $P' \equiv 1 + \beta P$ and $\Gamma \equiv 2\gamma_0/\alpha$. Thus, in the absence of phase transitions, $\ln T'$ is a linear function of $\ln P'$ with slope Γ.[4]) Note that at low pressure (compressions), (3) reduces to the Simon melting equation [1] which may be written as [12]

$$\ln (T_m/T_{m0}) = n \ln P' . \tag{4}$$

Extrapolation of the bulk modulus The procedure for extrapolating B_0 from a reference temperature, T_r, to the zero pressure melting temperature, T_{m0}, discussed in [12], required knowledge of the experimental values of B_0, $B_0' \equiv (\partial B/\partial P)_{P=0}$, and the volume coefficient of expansion, $a(T_r)$, at reference temperature T_r. In the case of NaCl and AgCl the required experimental values of $B_0(T_r)$ [16, 17], $B_0'(T_r)$ [16, 17], and $a(T_r)$ [16, 18] were available, and $B_0(T_{m0})$ could be calculated. The input $B_0(T_r)$ and resultant extrapolated $B_0(T_{m0})$ values for NaCl and AgCl are listed in Table 1. In the case of AgBr experimental values of the expansion coefficient were not available in the literature. Hence, for AgBr an extrapolated $B_0(T_{m0})$ value was obtained using the expansion coefficient data for AgCl. It is estimated that the extrapolated $B_0(T_{m0})$ value for AgBr, listed in Table 1, is accurate to within about $\pm 10\%$. It should be noted that even with this relatively inaccurate value for $B_0(T_{m0})$ one obtains an excellent fit to the experimental melting data for AgBr (see Table 3).

Results and discussion A nonlinear least squares fit was made to (3), assuming the $B_0(T_{m0})$ values given in Table 1 for NaCl, AgCl, and AgBr, and the β and Γ values listed in Table 2 were obtained. In Fig. 1 we have plotted $\ln T'$ versus $\ln P'$ for the NaCl [19], AgCl [20], and AgBr [20] melting data together with the results of the nonlinear least squares fit (solid line). Note that to a good approximation, $\ln T'$ is a linear function of $\ln P'$. In Fig. 2, the melting temperature, T_m, is plotted versus the pressure, P; the circles are the experimental

Table 2
Fitting constants

	β	Γ
NaCl	0.08397006	0.3702107
AgCl	0.08788295	0.2322001
AgBr	0.09636053	0.2597440

[4]) In the case where the solid undergoes a phase transition at pressure P_0 we showed in [12] that the reduced temperature satisfies the modified melting relationship, $\ln T' = \Gamma_2 \ln P_2'$, in the higher pressure phase, where $P_2' \equiv 1 + \beta_2(P - P_0)$.

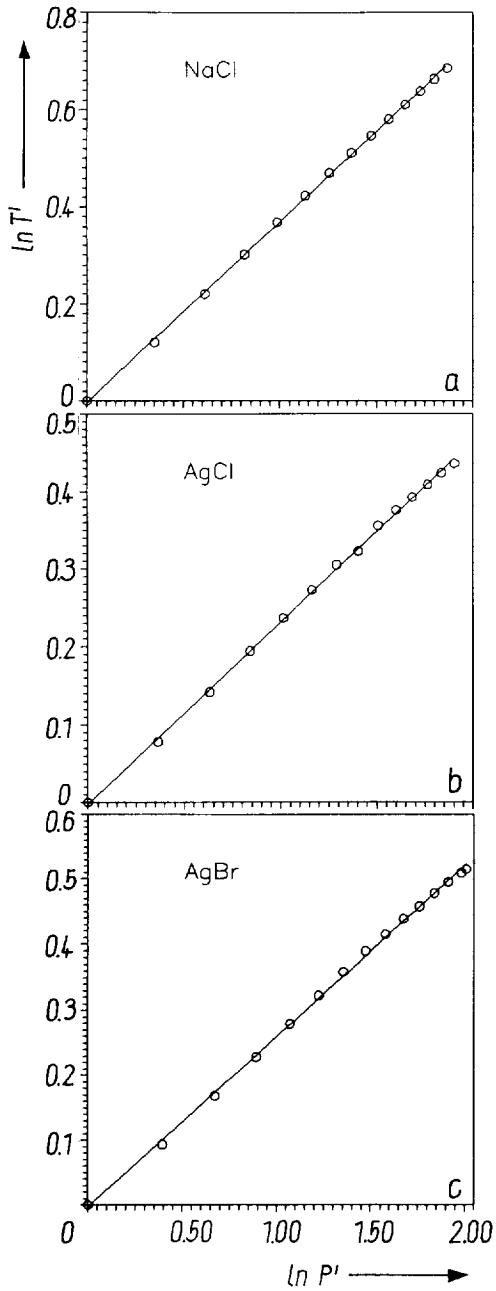

Fig. 1

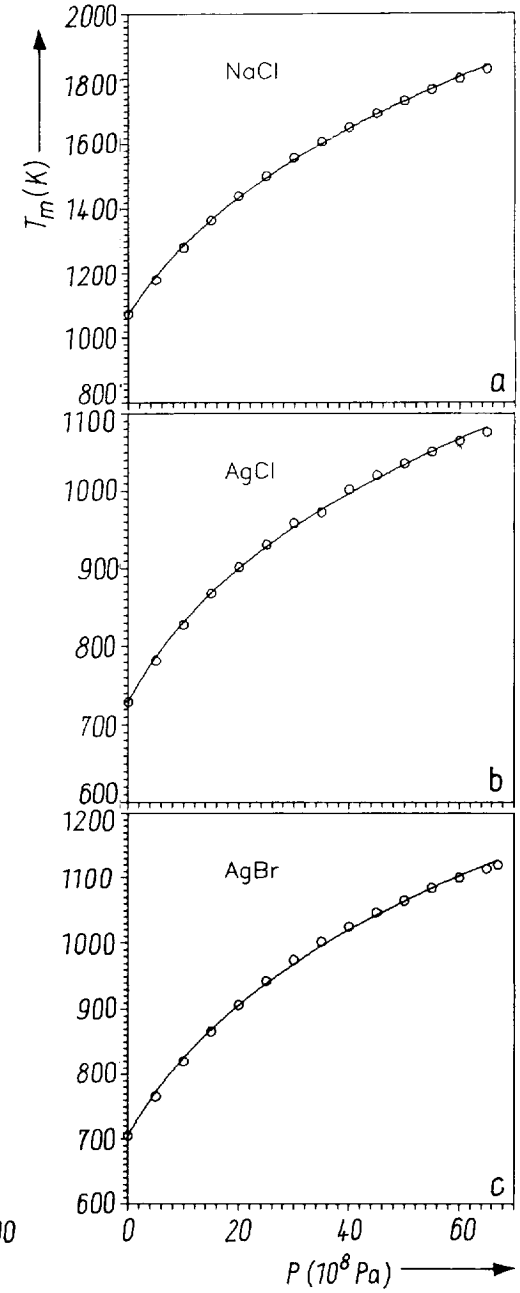

Fig. 2

Fig. 1. ln T' vs. ln P', $T' \equiv T_m/(T_{m0}X^2)$, $P' \equiv (1 + \beta P)$, and $X \equiv (V/V_0)^{1/3}$. a) ○ NaCl [19]; b) ○ AgCl [20]; c) ○ AgBr [20]; ——— equation (3)

Fig. 2. Melting temperature vs. pressure. a) ○ NaCl [19]; b) ○ AgCl [20]; c) ○ AgBr [20]; ——— theory

Table 3
Melting data

P (10^8 Pa)	NaCl [19]			AgCl [20]			AgBr [20]		
	T_m^{exp} (K)	T_m^t (K)	T_m^s (K)	T_m^{exp} (K)	T_m^t (K)	T_m^s (K)	T_m^{exp} (K)	T_m^t (K)	T_m^s (K)
0	1073.6	1073.6	1073.6	729.6	729.6	729.6	705	705	705
5	1179	1191.0	1188.3	782	787.0	787.3	766	773.1	773.6
10	1277	1284.0	1280.8	828	831.8	832.5	820	825.7	826.8
15	1363	1364.0	1359.3	868	868.9	869.9	866	869.2	870.8
20	1438	1432.8	1428.1	902	900.7	902.0	907	906.5	908.6
25	1500	1494.0	1489.5	931	928.7	930.4	943	939.3	941.9
30	1556	1549.2	1545.3	959	953.8	955.8	975	968.4	971.9
35	1605	1599.8	1596.6	973	976.6	978.9	1002	995.5	998.9
40	1650	1646.4	1644.1	1003	997.4	1000.0	1025	1020.0	1023.9
45	1692	1689.8	1688.4	1021	1016.8	1019.7	1047	1042.8	1047.1
50	1731	1730.4	1730.1	1036	1034.8	1037.9	1065	1064.0	1068.7
55	1767	1768.5	1769.4	1051	1051.7	1055.1	1084	1083.8	1088.9
60	1800	1804.6	1806.7	1065	1067.6	1071.2	1100	1102.6	1108.1
65	1829	1838.8	1842.2	1076	1082.6	1086.5	1114	1120.3	1126.1
67							1120	1127.2	1133.2

Note: T_m^t fit with (3), T_m^s Simon equation fit.

data and the solid line is a plot of the theoretical T_m versus P curve generated from the Γ and β values tabulated in Table 2. In Table 3 the theoretical melting temperatures calculated with the Γ and β values from (3) and with the n[5]) and β values from the Simon's equation (4) are compared with the experimental melting data [19, 20]. We observe that the difference between the experimental and theoretical melting temperatures calculated from (3), is less than 1% over the entire pressure range. This accuracy is achieved even for AgBr where a relatively inaccurate value for $B_0(T_{m0})$ was used, i.e. $\approx \pm 10\%$, as noted in the previous section. Note that (3) yields a better fit to the experimental melting data than the Simon equation, especially at pressure greater than about 50×10^8 Pa. (We obtain mean square deviations of 6.24×10^8 Pa versus 8.07×10^8 Pa for NaCl, 3.96×10^8 Pa versus 4.81×10^8 Pa for AgCl, and 5.08×10^8 Pa versus 6.66×10^8 Pa for AgBr.)

In conclusion, we have shown that the pressure dependence of the melting temperature of the primarily ionically bonded solids NaCl, AgCl, and AgBr may be accurately characterized by the relationship which was originally derived for metals [12], and which was subsequently shown to be valid for rare-gas solids [13]. Hence, the same melting relationship may be used to accurately characterize the pressure variation of the melting temperature for a variety of solids with different types of binding (i.e. metals, rare-gas solids, partially and primarily ionically bonded solids).

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[5]) $n = 0.289476$ for NaCl, $n = 0.2091627$ for AgCl, and $n = 0.2362146$ for AgBr.

References

[1] F. E. SIMON and G. Z. GLATZEL, Z. anorg. allg. Chem. **178**, 309 (1929).
[2] E. S. RAJA GOPAL, S. N. VAIDYA, R. D.- GAUIBHIR, and K. GOVINDARAJAN, J. Indian Inst. Sci. **49**, 61 (1967).
[3] E. A. KRAUT and G. C. KENNEDY, Phys. Rev. **151**, 668 (1966).
[4] S. N. VAIDYA and E. S. RAJA GOPAL, Phys. Rev. Letters **17**, 635 (1966).
[5] J. J. GILVARRY, Phys. Rev. Letters **16**, 1089 (1966).
[6] S. E. BABB, JR., Phys. Rev. Letters **17**, 1250 (1966).
[7] M. MUKHERJEE, Phys. Rev. Letters **17**, 1252 (1966).
[8] R. P. COUCHMAN and C. L. REYNOLDS, JR., J. appl. Phys. **47**, 5201 (1976).
[9] G. PERRIN and M. DELANNOY-COUTRIS, J. Phys. Chem. Solids **46**, 117 (1985).
[10] M. KUMARI, K. KUMARI, and N. DASS, phys. stat. sol. (a) **99**, K23 (1987).
[11] M. KUMARI and N. DASS, phys. stat. sol. (b) **146**, 105 (1988).
[12] H. SCHLOSSER, P. VINET, and J. FERRANTE, Phys. Rev. B **40**, 5929 (1989).
[13] H. SCHLOSSER and J. FERRANTE, Phys. Rev. B **43**, 13305 (1991).
[14] H. SCHLOSSER, J. FERRANTE, and J. R. SMITH, Phys. Rev. B **44**, 9696 (1991).
[15] H. SCHLOSSER and J. FERRANTE, J. Phys.; Condensed Matter **1**, 2727 (1989).
[16] S. YAMAMOTO, I. OHNO, and O. L. ANDERSON, J. Phys. Chem. Solids **48**, 143 (1987).
[17] S. D. CHAURVEDI, R. C. DIXIT, and A. A. S. SANGACHIN, phys. stat. sol. (b) **147**, 115 (1988).
[18] Y. S. TOULOUKIAN, R. K. B. KIRBY, R. E. TAYLOR, and T. Y. R. LEE (Ed.), Thermophysical Properties of Matter, No. 13 in TPRC Data Series, Thermal Expansion, IFI/Plenum, New York 1977.
[19] J. AKELLA, S. N. VAIDYA, and G. C. KENNEDY, Phys. Rev. **185**, 1135 (1969).
[20] J. AKELLA, S. N. VAIDYA, and G. C. KENNEDY, J. appl. Phys. **40**, 2800 (1969).

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