Effects of Phonon Dispersion and Anharmonicity on Thermo-physical Properties of Solids

Wilfried B. Holzapfel

Department-Physik, Universität Paderborn, D-33095 Paderborn, Germany

Reprint requests to Prof. W. B. Holzapfel. E-mail: holzapfel@physik.upb.de

Z. Naturforsch. **2008**, *63b,* 718 – 724; received January 22, 2008

Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

Both phonon dispersion and anharmonicity contribute to the thermo-physical properties of solids in such a way that serious mistakes can be made, if these effects are not taken into account in the realization of semi-empirical equations of state (EOS) from limited experimental data sets. These effects are illustrated in comparisons of EOS data for different types of solids.

Key words: Equation of States (EOS), Lattice Dynamics, Phonon Dispersion, Anharmonicity, Thermo-physical Properties

Introduction

Accurate formulations for the equation of states (EOS) of all kinds of solids are needed in many different applications like in the area of geosciences [1], in the realization of a practical pressure scale [2 – 5] and more generally in all kinds of materials design. In all these cases one starts from limited data sets and uses some model with more or less well established assumptions to predict the behavior of solids in wide and often unexplored ranges of pressure and temperature. The simplest and least reliable approaches apply "parametric" EOS forms, which use a given analytic form like $p(V,T) = p(V,V_0(T),K_0(T),K_0'(T),\ldots)$ for an isotherm with temperature dependent "parameters" $V_0(T),K_0(T),K_0'(T),\ldots$ where $V_0(T)$ represents the temperature dependent volume at ambient (or zero) pressure, $K_0(T)$ is the temperature dependent bulk modulus at ambient (or zero) pressure and $K_0'(T)$ is its pressure derivative. Very often only simple power laws are used for the temperature dependence of these "parameters" without any theoretical foundation.

However, the thermo-physical properties of solids can be modelled much more reliably by using the thermodynamic approach, which starts from a reasonable model for the volume dependence of the ground-state (zero temperature or static lattice) energy $E_0(V)$ of the ideal lattice and adds appropriate terms to the free energy for the various (temperature dependent) excitations from phonons $F_{ph}(V,T)$, from the conduction electrons in metals (or semiconductors at very high temperatures) $F_{el}(V,T)$, and from lattice defects $F_{def}(V,T)$. Nevertheless many approximations have to be made in this approach, for instance that electron-phonon interactions can be neglected, and defects do not modify the phonon or electron contributions. In the present contribution, I will restrict myself to contributions from phonons, which are most commonly treated in the Mie-Grüneisen approximation [6, 7] which uses only one temperature independent (average) Grüneisen parameter for all the phonons. Models which go beyond the Grüneisen approximation may include effects from anharmonicity and dispersion of the mode Grüneisen parameters. When these effects are included, one obtains different intrinsically temperature dependent Grüneisen parameters for the thermal pressure and for the thermal expansion [1, 8 – 12].

Anharmonicity of the phonons has been taken into account already in many recent evaluations of thermo-physical properties, however, detailed studies and modelling of phonon dispersion are not so common. In fact, in a recent study on diamond [13] with theoretical data for the phonon dispersion, the question occurred whether the effects of anharmonicity and dispersion can be separated uniquely without further theoretical input just from an evaluation of all the given thermo-physical data at ambient pressure. To answer this question, I try in this study to evaluate both data for the metals Cu, Ag, and Au on the one hand and data for diamond on the other hand without the use of theoretical data on the dispersion of Grüneisen parameters to obtain more general recommendations also for other materials.

The Model

Like in our previous evaluations of EOS data [11, 14, 15], I use also here the Adapted Polynomial expansion APL of the form:

$$p_{APL} = 3K_0 x^{-5}(1-x)\exp\left(c_0(1-x)\right) \cdot \left(1 + x\sum_{2}^{L} c_k (1-x)^{k-l}\right)$$

but only to second order AP2, where K_0 represents the (isothermal) bulk modulus at ambient conditions, $x = \sqrt[3]{V/V_0}$ is a reduced length scale and $c_0 = -\ln(3 \cdot K_0/p_{FG0})$ with $p_{FG0} = a_{FG} \cdot (Z/V_0)^{5/3}$ stands for the pressure of a Fermi gas with the total electron number Z in the (atomic) volume V_0 with the Fermi-gas parameter $a_{FG} = 0.2337 GPa \cdot nm^5$ to guarantee the correct behavior at very high pressures. The second order parameter $c_2 = (3/2)(K_0' - 3) - c_0$ (with K_0' for the pressure derivative of the (isothermal) bulk modulus under ambient conditions) adds only a small contribution for regular solids, and the higher order parameters of this form of APL are all equal zero in the present second order approximation AP2. One may notice that AP2 serves as a very good approximation for cold p-V-isotherms of regular solids under strong compression and can be integrated also analytically to obtain the corresponding energy-volume relation [16].

The quasi-harmonic phonon contribution to the total free energy is treated in the optimized pseudo-Debye-Einstein (opDE2) approximation [8], which uses 3 characteristic temperature parameters TD, $TE1$, and $TE2$: the low temperature Debye temperature TD for the zone center phonon contribution, one Einstein term with $TE1$ for the remaining acoustic phonons, and one additional Einstein temperature $TE2$ for the optical phonons. In simple mono-atomic solids with no optical phonons the second Einstein parameter represents just the second half in the phonon density of states. Previously only one Einstein term (opDE1) was used for the mono-atomic solids Cu, Ag, and Au [11]. The use of opDE2 for these simple solids is more reasonable when one wants to take into account also dispersion in the mode Grüneisen parameters. In the simplest case one may use just two different average "mode" Grüneisen parameters, one γDa for all the acoustic modes and one γDo for the "optic" modes. This means that a fixed correlation of the first Einstein parameter $TE1 = fE1 \cdot (3/4) \cdot TD$ to the low temperature Debye temperature TD is used with an optimized correlation parameter $fE1 = 0.80$. With the weight $g = 0.040$ for the pseudo-Debye contribution one obtains then for the "acoustic" Debye temperature $TDa = TD \cdot (g + (1-g) \cdot fE1)$ and for the high-temperature Debye temperature $TDh = (TDa + TDo)/2$ with the "optic" Debye temperature $TDo = fE2 \cdot (3/4) \cdot TD$. The reduced quasi-harmonic specific heat capacity c_{qh} of this opDE2 model has the form:

$$c_{qh}(T, TD, TE1, TE2) = \frac{g \cdot \left(\frac{T}{TD}\right)^3 \cdot \left(4 \cdot a_0 \cdot g + \left(\frac{T}{DT}\right)^3\right)}{2 \cdot \left(a_0 \cdot g + \left(\frac{T}{TD}\right)^3\right)^3} + \frac{1-g}{2} \cdot cE\left(\frac{T}{TE1}\right) + \frac{1}{2} \cdot cE\left(\frac{T}{TE2}\right)$$

with the weight $g = 0.040$ and the parameter $a_0 = 0.0434$ in the pseudo-Debye term. The two Einstein terms have the (normalized) form

$$cE\left(\frac{T}{TE}\right) = \left(\frac{TE}{2 \cdot T}\right) \cdot \sinh\left(\frac{TE}{2 \cdot T}\right).$$

The correlation between TD and $TE1$ stabilizes the fits of c_V-data significantly. The low temperature behavior determines TD and the related parameter TDa. The variation at moderate temperatures gives both $TE2$ and TDo and hence with TDa also TDh. Finally at high temperatures a small anharmonic phonon contribution must be added. Additional contributions from defects [17] are neglected here. This leaves one parameter Aph for the quartic anharmonicity at ambient pressure and one additional parameter $f6$ for the relative strength of all the higher-order contributions. A theoretical modelling on the basis of a classical mean field theory with quantum corrections [10] determines the volume dependence of this anharmonicity in the present approach. Dispersion in the Grüneisen parameters is usually not needed in the fits of the c_V-data at ambient pressure. The anharmonic contribution is noticed as a small deviation from the classical value of 3k/atom at very high temperatures. However, the variation of the thermal expansion at ambient pressure, $V_0(T)$, the thermal volume expansion coefficient, $\alpha_{V0}(T)$, and especially the bulk modulus $K_0(T)$ at (ambient) pressure

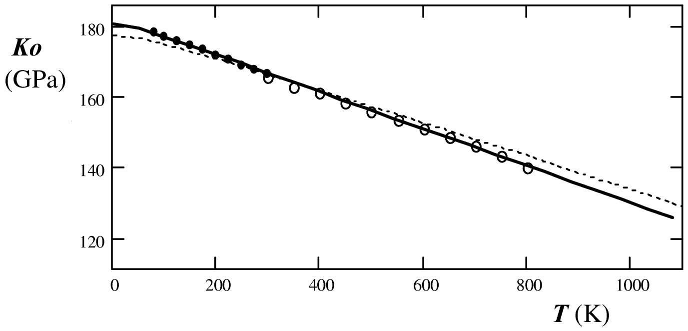

Fig. 1. Effect of temperature on the bulk modulus of Au at ambient pressure. Solid dots and circles represent experimental data from the literature [24 – 26]. The dotted line shows the pure volume dependence without phonon contributions. The solid line represents the result from the opDE2 fit.

are strongly affected by both anharmonicity and dispersion as we will see later.

Comparison with Experimental Data

At first I repeated the evaluation of all the thermo-physical data for Cu, Ag, and Au with the present opDE2 model for the phonons instead of opDE1 in the previous study [10, 11]. The splitting of the phonon spectrum into more phonons contributing now to TDa in opDE2 than to the previous TD in opDE1 results in a minor improvement of the fits and in minor changes of the values for the phonon parameters as shown in Table 1, where the first column of the phonon parameters corresponds in each case to the values for opDE1 and the second column to opDE2. The different meaning of TDa results apparently in more significant changes in the values for the anharmonicity parameters Aph and $f6$ which means that these values are indeed sensitive to small deficiencies in the representation of the phonon density of states (DOS) of both models, opDE1 and opDE2. Since these anharmonic contributions decrease rapidly under pressure, these minor deficiencies do not affect the representation of the thermo-physical data seriously. Within the given precision the values for the single (average) Grüneisen parameter of these fits do not change for Cu and Ag, and for Au the change is only marginal. Attempts to use two different Grüneisen parameters (dispersion) γDa and γDo for the lower and upper half of the phonon DOS did not improve the quality of these fits significantly. In fact, the behavior of the phonon contribution for Cu, Ag, and Au is so regular that even the Barton-Stacey approximation for the volume dependence of the average phonon Grüneisen parameter [18] was perfect within the uncertainties of these fits as illustrated in Fig. 1 just for the temperature dependence of the bulk modulus of Au at ambient pressure. One may notice by comparison of the dotted line for the pure volume dependence of the bulk modulus at r. t. with the solid line including the phonon contribution that the total phonon contribution is very small and gives a strong constraint on the pressure derivative of the bulk modulus under ambient conditions. If cross-calibrations with EOS data from other materials would change slightly the K_0' values given in Table 1, very small contributions from dispersion in the Grüneisen parameters or deviations from the Barton-Stacey constraint could possibly compensate for such changes. In fact, also all the other thermo-physical data for Cu, Ag, and Au are equally well represented by the present opDE2 fit, which shows no visible changes with respect to the results in the corresponding Figures given previously [11].

Table 1. Thermo-physical parameters for Cu, Ag, and Au.

	Cu		Ag		Au	
Z	29		47		79	
M	63.55		107.87		196.97	
$TFeff$, K	57213		62220		55626	
Vr, cnm	11.814		17.056		16.964	
Kr, GPa	133.1		101.0		166.4	
$K'r$	5.40		6.20		6.21	
TDa, K	330	335	214	216	160	167
TDh, K	328	305	223	208	183	169
γr	2.00	2.00	2.46	2.46	3.11	3.09
$1000 \times Aph$	2.11	1.51	3.07	3.30	3.87	3.62
$f6$	8.0	5.0	0.80	1.10	1.58	1.48

For diamond, however, the situation is very different: Theoretical studies [21, 13] show negative thermal expansion and negative acoustic mode Grüneisen parameters at elevated pressure with the implication that dispersion should be significant for the EOS of diamond in wide ranges of pressure and temperature. A recent formulation of a semiempirical EOS for diamond included anharmonicity but neglected dispersion completely [12]. From this point of view, it was most interesting to fit all thermo-physical properties of diamond with the present opDE2 approach including both

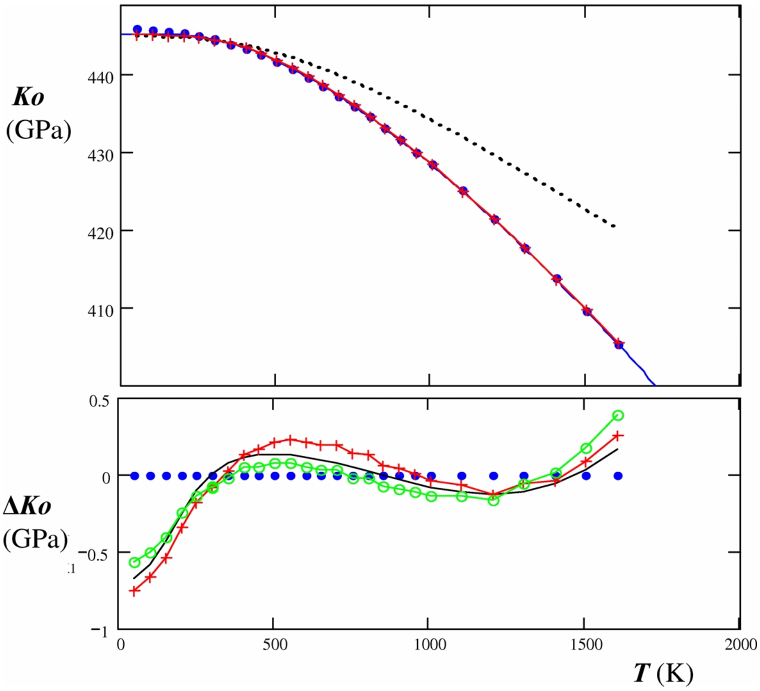

Fig. 2. Effect of temperature on the bulk modulus of diamond at ambient pressure and difference of the fits with respect to the experimental data. Solid dots represent experimental data from the literature [19, 20]. The dotted line shows the pure volume dependence without phonon contributions. The thin solid line results from the parametric fit. Lines with crosses and circles represent the results from opDE2 fits with and without dispersion, respectively.

anharmonicity and dispersion for a comparison with the seemingly simpler procedure used previously [12]. Various fits of the experimental data for $K_0(T)$ of diamond are illustrated in Fig. 2 together with the pure volume dependence of the bulk modulus at ambient temperature using the most reasonable value [5, 22, 23] for $K_0' = 3.65(5)$ illustrated by the dotted line. The obviously smoothed experimental data [24–28] are shown as solid dots. The solid line reproduces a polynomial fit in terms of the internal energy. The thin line with crosses represents the fit with phonon dispersion and the additional thin line with circles in the difference plot shows the fit without phonon dispersion. This fit uses the Altshuler form [29] for the average Grüneisen parameter:

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)\,(V/V_0)^q$$

whereby the exponent $q = (1 - \gamma_\infty/\gamma_0) \cdot \Gamma_0$ is related to the value of the logarithmic volume derivative $\Gamma = \ln\gamma/\ln V$ at ambient pressure, and γ_∞ represents the limiting value of γ at infinite compression. This Altshuler form was used here for comparison with a recent fit of the diamond data with this same form [12].

In the fit with two different mode Grüneisen parameters, γDa for all the acoustic modes and γDo for the optic modes, the Altshuler form was used for the volume dependence of the optic mode; however, since this form can not reproduce a maximum in the volume dependence of γ, the more flexible form of Bushman-Lomonosov-Fortov [30]:

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)\,(V/V_0)\,\left(V_0^2 + V_m^2\right) / \left(V^2 + V_m^2\right)$$

with $\gamma_\infty = 2/3$ and the new parameter $V_m = V_0\sqrt{1 + 2\Gamma_0\gamma_0/(\gamma_0 - \gamma_\infty - \Gamma_0\gamma_0)}$ was used for the fit of Γ_0.

First of all one may notice in Fig. 2 that the phonon contribution to the temperature dependence of $K_0(T)$ is very large in comparison with Fig. 1 for Cu, Ag, and Au. A smaller phonon contribution would be obtained for larger values of K_0', but a complete reduction of the phonon contribution would require an unreasonably large value of $K_0' = 5.7$. The strong phonon contribution requires here in the Altshuler form of the average Grüneisen parameter a very large $\Gamma_0 = 2.21$ in comparison with the value of $\Gamma_0 = 0.35$ calculated in the Barton-Stacey approximation.

Fig. 2 indicates that the fit with dispersion represented by the thin line with crosses appears to be not as good as the fits without dispersion or the simple adapted polynomial. Since all the fits show very similar systematic deviations from the experimental data, it seems to be possible that the analytical smoothing

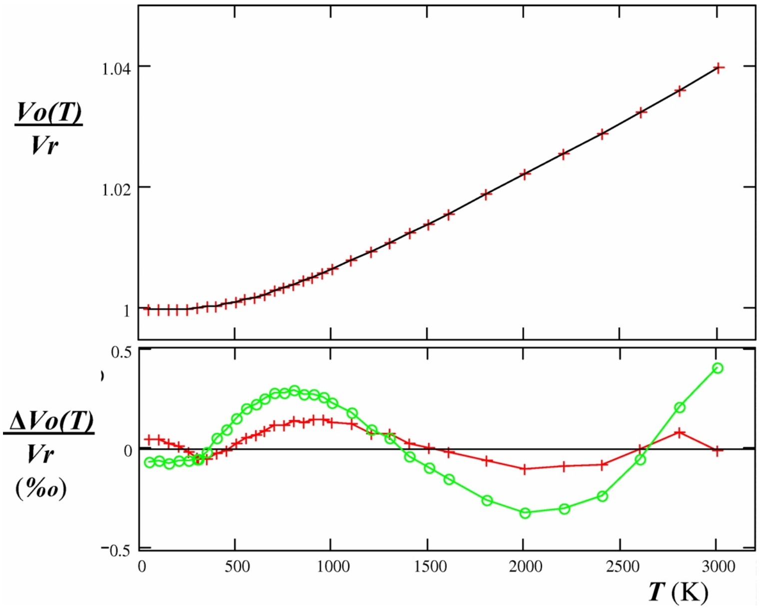

Fig. 3. Effect of temperature on the volume of diamond at ambient pressure. The thin curve reproduces the experimental data from the literature [31]. Lines with crosses and circles represent the results from opDE2 fits with and without dispersion, respectively.

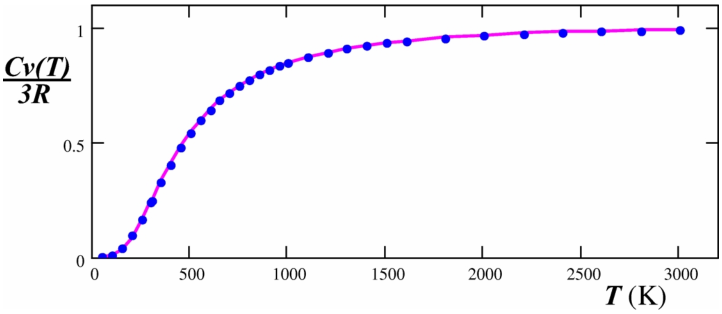

Fig. 4. Effect of temperature on the normalized, constant volume heat capacity of diamond at ambient pressure. The dots reproduce the experimental data from the literature [31]. The line represents the results from the opDE2 fit.

of the experimental data by a simple polynomial in temperature is responsible for most of these systematic deviations. On the other hand, one can see in the difference plot of the thermal expansion given in the lower part of Fig. 3 that opDE2 with dispersion (line with crosses) fits significantly better than without dispersion (line with circles). The slight systematic deviations from the smoothed experimental data [29] may result from slight deficiencies of the opDE2 model, which uses only 5 phonon parameters (in the case without dispersion) in comparison with the 15 phonon parameters used in the latest fit [12] (without dispersion).

The fit of the experimental c_V-data for diamond at ambient pressure [31] with anharmonic contributions and dispersion in the opDE2 model is shown in Fig. 4. The quality of this fit looks as good as the smoothed data, and the close approach towards the classical value of 1 at high temperatures indicates in this scaled representation that the anharmonic contributions are very small in this case.

Results

The results for the opDE2 fits of all the thermophysical data with and without dispersion in the Grüneisen parameters are illustrated in Fig. 5:

1) The fit with the Altshuler form for the average γ (without dispersion) gives the line of solid dots, which varies much more strongly near ambient pressure than the (regular) Barton-Stacey approximation (thin dashed line).

2) The difference in the fitted average Grüneisen parameters for the optic and acoustic modes, γDo and γDa, is very large at ambient pressure as shown by the upper and lower solid curve at the value 1 for the relative volume. Since the constraint for this splitting in the

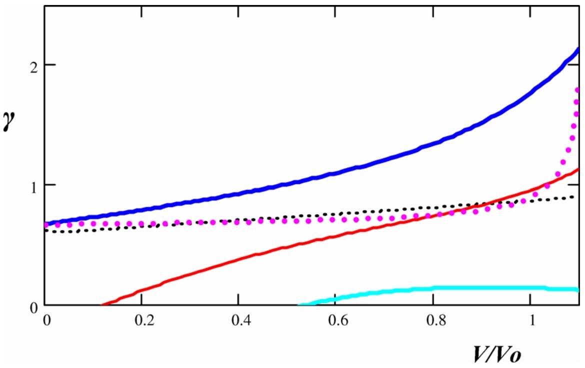

Fig. 5. Volume dependence of the various Grüneisen parameters for diamond discussed in the text.

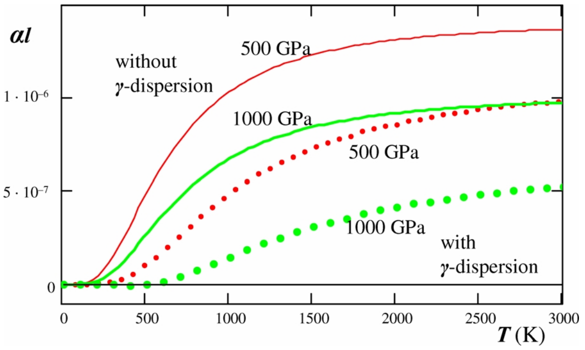

Fig. 6. Temperature dependence of the linear thermal expansion coefficient calculated for diamond in the opDE2 model with and without dispersion, respectively.

fits is not very strong and shows a flat minimum in the goodness of the fit, the result presented in Fig. 5 by the solid curves may be considered as an upper boundary for the contribution from dispersion.

3) The average of γDo and γDa is represented by the thinner line in between these two curves. The value of this average Grüneisen parameter near ambient conditions is not much different from the value given also by the dotted curve; however, the slope is much more moderate than for the fit without dispersion.

4) Since the fit of the ambient pressure data involves only the range from 1 to 1.04 in volume expansion, the variation of the Grüneisen parameters outside the fitted region is not well constrained by the experimental data. γ_∞ for the optical γDo and for the Altshuler form without dispersion is only constrained to values smaller than the respective value under ambient conditions and has been fixed therefore just to the theoretical value $\gamma_\infty = 2/3$.

5) Similarly, the value of γDa under strong compression is not well constrained by the experimental data, however, the theoretical prediction [21] of a negative thermal expansion above about 700 GPa is only reproduced when dispersion with negative values for γDa in this region is used.

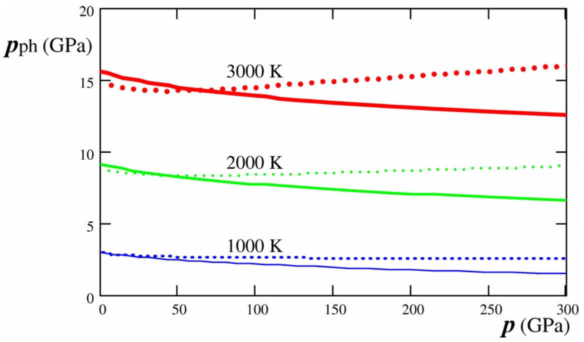

Fig. 7. Pressure dependence of the thermal pressure for diamond at different temperatures calculated in the opDE2 model with and without dispersion (solid and dotted lines), respectively.

Results for the linear thermal expansion coefficient of diamond under strong compression from the present opDE2 model with and without dispersion are shown in Fig. 6 for 500 GPa and also for 1 TPa. Although the variation with dispersion is adjusted to the theoretical prediction [21], one can see that a model without dispersion gives only positive values for this range.

With respect to practical applications it is more interesting to look at the difference in thermal pressure illustrated in Fig. 7. While the differences in the thermal pressure remain rather small below 100 GPa, one can notice very significant differences at higher pressures already at temperatures in the range of 1000 K.

Conclusion

Thermo-physical properties of solids under strong compression can be affected very strongly by phonon dispersion even in “simple” solids like diamond. Since diamond and diamond-like materials like wurzite-type and zinc-blend-type BN have been considered as reference materials for pressure (and temperature) determination under strong compression more attention should be paid to the effects of dispersion and not only to anharmonicity in these and similar cases.

Acknowledgement

I would like to thank Gérard Demazeau here for many stimulating discussions on properties of solids under pressure and for the many other stimulating events.

[1] J.-P. Poirier, *Introduction to the Physics of the Earth's Interior*, Cambridge University Press, Cambridge **2000**.

[2] V. E. Bean, S. Akimoto, P. M. Bell, S. Block, W. B. Holzapfel, M. H. Manghnani, M. F. Nicol, S. M. Stishov, *Physica* **1986**, *139 & 140 B*, 52.

[3] I. V. Aleksandrov, A. F. Goncharov, A. N. Zisman, S. M. Stishov, *Sov. Phys. JETP* **1987**, *66*, 384.

[4] W. B. Holzapfel, in *High Pressure Techniques in Chemistry and Physics* (Eds.: W. B. Holzapfel, N. Isaacs), Oxford University Press, Oxford **1997**, p. 47.

[5] W. B. Holzapfel, *High Press. Res.* **2005**, *25*, 87.

[6] E. Grüneisen, *Ann. d. Phys. (Leipzig)* **1912** *IV*, *39*, 257.

[7] E. Grüneisen, in *Handbuch der Physik*, Vol. X (Eds.: H. Geiger, K. Scheel) **1926**, p. 1.

[8] W. B. Holzapfel, in *High-Pressure Crystallography* (Eds.: A. Katrusiak, P. McMillan), Kluwer Academic Publishers, Dordrecht **2004**, p. 217.

[9] W. B. Holzapfel, *High Press. Res.* **2005**, *25*, 187.

[10] W. B. Holzapfel, *High Press. Res.* **2006**, *26*, 313.

[11] W. B. Holzapfel, M. F. Nicol, *High Press. Res.* **2007**, *27*, 377.

[12] P. I. Dorogokupets, A. R. Oganov, *Phys. Rev. B* **2007**, *75*, 024115.

[13] W. B. Holzapfel, J. S. Tse, unpublished results.

[14] W. B. Holzapfel, *High Press. Res.* **1991**, *7*, 290.

[15] W. B. Holzapfel, *Z. Kristallogr.* **2001**, *216*, 473.

[16] W. B. Holzapfel, *Phys. Rev. B* **2003**, *67*, 026102.

[17] P. I. Dorogokupets, *Petrology* **2001**, *9*, 534.

[18] M. A. Barton, F. D. Stacey, *Phys. Earth Planet. Inter.* **1985**, *39*, 167.

[19] Y. A. Chang, L. Himmel, *J. Appl. Phys.* **1966**, *37*, 3567.

[20] J. S. Tse, W. B. Holzapfel, *J. Appl. Phys.* **2008**, in press.

[21] J. Xie, S. P. Chen, J. S. Tse, S. de Gironcoli, S. Baroni, *Rev. Rev. B* **1999**, *60*, 9444.

[22] K. Kunc, I. Loa, K. Syassen, *Phys. Rev. B* **2003**, *68*, 094107.

[23] K. Kunc, I. Loa, K. Syassen, *High Press. Res.* **2004**, *25*, 101.

[24] H. J. McSkimin, W. L. Bond, *Phys. Rev.* **1957**, *105*, 116.

[25] H. J. McSkimin, P. Andreatch, *J. Appl. Phys.* **1972** *43*, 2944.

[26] M. Grimsditch, A. K. Ramdas, *Phys. Rev. B* **1975**, *11*, 3139.

[27] E. S. Zouboulis, M. Grimsditch, A. K. Ramdas, S. Rodriguez, *Phys. Rev. B* **1996**, *54*, 3989.

[28] M. Grimsditch, in *Properties, Growth and Application of Diamond* (Eds.: M. H. Nazaré, A. J. Neves) INSPEC, London **2001**, p. 28.

[29] L. V. Altshuler, S. E. Brusnikin, E. A. Kuzmenov, *Zh. Prikl. Mekh. Tekh. Phys.* **1987**, *161*, 134.

[30] A. V. Bushman, I. V. Lomonosov, V. E. Fortov, *Sov. Tech. Rev. B. Therm. Phys.* **1993**, *5*, 1.

[31] R. R. Reeber, K. Wang, *J. Electr. Mater.* **1996**, *25*, 63.