Journal of Thermal Analysis, Vol. 21 (1981) 309–326

ANALYSIS OF THE HEAT CAPACITIES OF GROUP IV CHALCOGENIDES USING DEBYE TEMPERATURES

U. GAUR, G. PULTZ, H. WIEDEMEIER and B. WUNDERLICH

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181, U.S.A.

(Received December 18, 1980)

The low temperature heat capacities of 13 group IV chalcogenides are examined. The heat capacity of crystals with largely isotropic structure (GeTe, SnSe, SnTe, PbS, PbSe, PbTe) can be represented within $\pm 3\%$ by a three-dimensional Debye function ($\theta_3 = 205$, 230, 175, 225, 150 and 130, respectively). The heat capacity of crystals with anisotropic structures (GeS, GeSe, SnS, GeS_2 and SnS_2) could only be represented by pairs of two-dimensional Debye functions for the longitudinal and transverse lattice vibrations (error ± 0.5 to 3%; $\theta_2(l) = 505$, 345, 400, 705, 480 and 570, respectively, and $\theta_2(t) = 200$, 185, 160, 175, 100 and 265, respectively).

Since the two-dimensional Debye function has not been tabulated in detail, we offer in the appendix a five place table of it. Raman and infrared data support this analysis.

Low temperature heat capacities are often well described by the Debye approach [1]. In extensive reviews [2, 3] it was shown earlier that a single θ-temperature could represent the heat capacity at constant volume for many elements and simple compounds adequately up to about 3θ. For two-dimensional and one-dimensional crystals, analogous two-dimensional and one-dimensional Debye functions can be derived [4–6]. The one-dimensional Debye function alone and in combination with a three-dimensional Debye function (Tarasov function) found widespread application in the description of heat capacities of linear macromolecules [7]. Two-dimensional Debye functions were used to described heat capacities for crystals with layer structures such as graphite and boron nitride [4, 6, 8]. Tables of the Debye functions, which are somewhat cumbersome to calculate, are widely available for the three-dimensional case [9]. A one-dimensional Debye function table was published by us earlier [10]. Since there seems to be no tabulation [11] of a precision two-dimensional Debye function table, we included such a table in the appendix.

The class IV chalcogenide crystals fall into two groups. One has a largely isotropic crystal structure, the other a layer-type structure. It will be shown that the model for heat capacity description must take, as expected, this fact into account.

Our initial interest in group IV chalcogenides arose from the study of vapor transport properties [12, 13]. For the interpretation of these, accurate values of enthalpies, entropies and Gibbs free energies are needed. Since heat capacities are usually not available to the lowest temperatures, we undertook the present study which includes 13 different group IV chalcogenides (see Table 1).

Table 1

Group IV chalcogenides and their low temperature heat capacity expressions

Compound	Crystal structure	C_p references	A_0^a for Θ_3 (Kmol/J) $\times 10^3$	Θ_3	% Error in C_V from Θ_3	$\Theta_2(t)$	$\Theta_2(l)$	% Error in C_V from Θ_2
GeS	orthorhombic (double-layers)	16, 17, 22	—	—	—	200	505	$<\pm 2.0$[d]
GeGe	orthorhombic (double-layers)	16, 17, 22	5.12	270	$<\pm 2.0$[b]	185	345	$<\pm 0.5$
GeTe	rhombohedral	17, 18, 20	10.24	205	$<\pm 1.0$[b]	—	—	—
SnS	orthorhombic (double-layers)	23	5.12	300	$<\pm 2.0$[b]	160	400	$<\pm 3.0$[d]
SnSe	orthorhombic (double-layers)	21	10.24	230	—[c]	—	—	—
SnTe	cubic	20	5.12	175	—[c]	—	—	—
PbS	cubic	19	5.12	225	$<+0.5$[b]	—	—	—
PbSe	cubic	19	5.12	150	$<\pm 3.0$[b]	—	—	—
PbTe	cubic	19	5.12	130	$<\pm 2.0$[b]	—	—	—
$GeSe_2$	orthorhombic (double-layers)	24	—	—	—	175	705	$<\pm 3.0$[d]
$GeSe_2$	orthorhombic (double-layers	24	—	—	—	100	480	$<\pm 1.0$[d]
SnS_2	hexagonal (triple-layers)	23	—	—	—	265	570	$<\pm 1.5$[d]
SnSe	hexagonal (triple-layers)	21	—	—	—	—	—	—

[a] per mole of atoms
[b] from 100K to 250K
[c] insufficient data to determine θ accurately
[d] for 50K to 250 K
[e] no data available below 220 K

Application of the three-dimensional Debye function

The analysis of heat capacities of group IV–VI compounds below 200 K is based on five approximation methods: The addition of contributions of the constituent elements [14, 15], the use of the Debye model [16–21], the application of a combined Debye and Einstein model [14, 22, 23], the fit to the Tarasov model [16], and the approximation to an exponential function ($C_p = AT^n$) [16, 18, 24]. Most of these analyses had little or no structural justification.

We began our analysis with the application of the three-dimensional Debye model

$$C_v = 9Nk \quad 4\left(\frac{T}{\theta_3}\right)^3 \int_0^{\Theta_3} \frac{x^3 dx}{e^x - 1} - \frac{\theta_3/T}{e^{(\Theta_3/T} - 1} \tag{1}$$

or abbreviated, for one mole of vibrators

$$C_v = 3RD_3(\theta_3/T) \tag{2}$$

The expression $D(\theta_3/T)$ is the three-dimensional Debye function, θ_3 is the three-dimensional Debye temperature, and x represents $h\nu/kT$. The relationship between the measured C_p and C_v is

$$C_p - C_v = \alpha^2 VT/k \tag{3}$$

where α is the isothermal expansivity, K is the isothermal compressibility and V is the molar volume of the solid. Since α and K are not commonly measured, and are not available for the group IV chalcogenides, we assume as a first approxima-

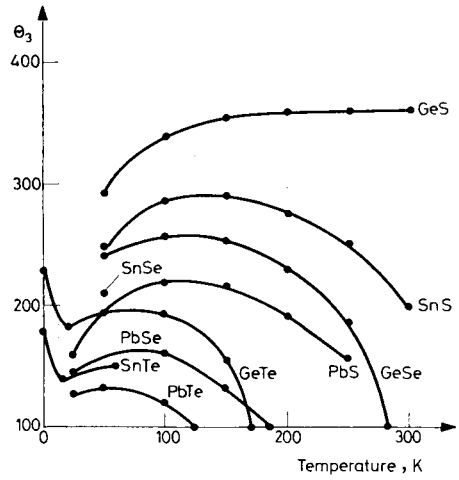

Fig. 1. θ_3 as a function of temperature for group IV monochalcogenides. θ_3 was calculated from C_p

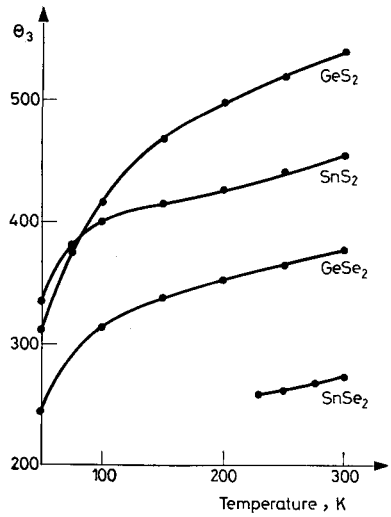

Fig. 2. θ_3 as a function of temperature for group IV dichalcogenides. θ_3 was calculated from C_p

tion, that up to 300 K C_p is essentially equal to C_v. A plot of calculated θ_3 values from the experimental C_p values for the various group IV chalcogenides is shown in Figs 1 and 2. All group IV chalcogenides show considerable variation in θ_3 with temperature, as indication of serious shortcomings of the approach. The decrease in θ_3 with increasing temperature occurs when C_p approaches the upper limit for C_v of $6R$ for binary compounds or of $9R$ for ternary compounds. In this temperature range the θ_3 calculation is particularly sensitive to the difference between C_p and C_v. As a second approximation we employed several methods to estimate the $C_p - C_v$ difference and corrected the θ_3 calculation. A commonly used approximation was introduced by Nernst and Lindemann [25]. For elements and ionic solids they suggest

$$C_p - C_v = A_0 \cdot C_p^2 T/T_m , \tag{4}$$

where T_m is the melting temperature and A_0 is a constant determined to be $5.12 \times \times 10^{-3}$ K mol/J. (Note that this constant is defined per mole of atoms.) Nernst and Lindemann show in their listed values of A_0 a variation from 2.4×10^{-3} to 9.6×10^{-3} K mol/J [25]. Changing the experimental C_p values with the help of Eq. 4 into C_v leads to the θ_3 values plotted in Figs 3 and 4. Some of the monochalcogenides show now a largely constant θ_3 value with only minor fluctuations (particularly the lead chalcogenides, GeSe and SnS), while GeS and the dichalcogenides (Fig. 4) still show extensive variation of θ_3 with temperature.

As mentioned above, the error in A_0 is about $\pm 50\%$. Allowing A_0 to go to its upper limit, $C_p - C_v$ was recalculated and θ_3 values obtained. These are shown in Figs 5 and 6. In this case, θ_3 is practically temperature independent for the

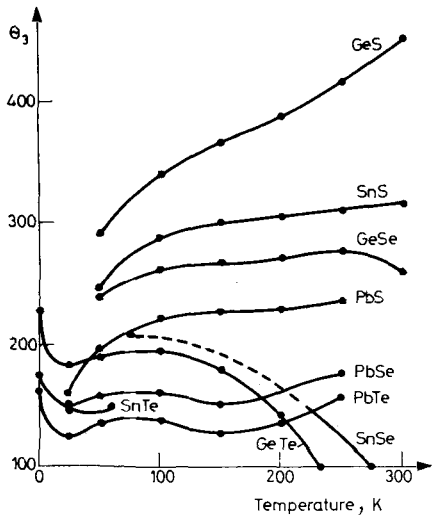

Fig. 3. θ_3 as a function of temperature for group IV monochalcogenides. Θ_3 was calculated from C_v using the Nernst–Lindemann approximation with $A_0 = 5.12 \times 10^{-6}$ K mol/J

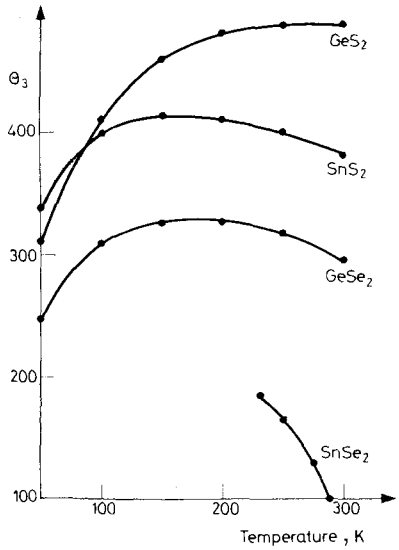

Fig. 4. θ_3 as a function of temperature for group IV dichalcogenides. θ_3 was calculated from C_v determined by the Nernst–Lindemann approximation with $A_0 = 5.12 \times 10^{-6}$ K mol/J

additional compounds GeTe and SnSe. The previously shown temperature independence of θ_3 for GeSe and SnS (Fig. 3) now reveals a considerable increase of θ_3 with temperature. The corresponding behaviour of the dichalcogenides is even

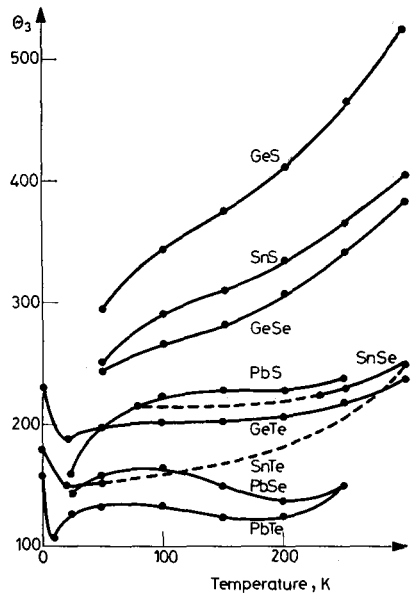

Fig. 5. θ_3 as a function of temperature for group IV monochalcogenides. Θ_3 was calculated from C_v determined by the Nernst–Lindemann approximation with $A_0 = 1.02 \times 10^{-2}$ K mol/J

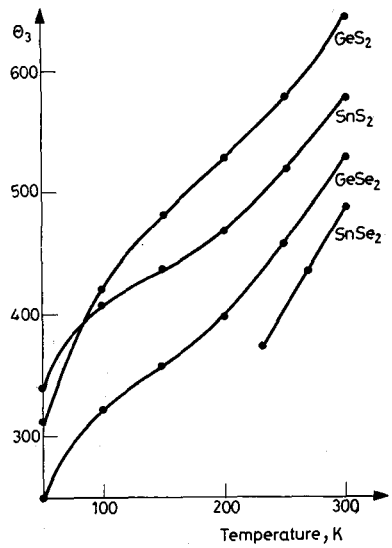

Fig. 6. θ_3 as a function of temperature for group IV dichalcogenides. Θ_3 was calculated from C_v determined by the Nernst–Lindemann approximation with $A_0 = 1.02 \times 10^{-2}$ K mol/J

more pronounced (Fig. 6). To test the validity of the Nernst–Lindemann approximation, we looked for experimental data to use in Eq. 3. Data were only available for GaSe [26], which exhibits a layer-type crystal structure similar to some group IV compounds. The $C_p - C_v$ difference was found to be about one half the value predicted by the Nernst–Lindemann equation. (Note that values calculated by Aliev *et al.* [26] for GaSe using the Nernst–Lindemann expression are too large by a factor of two since they use A_0 "per atom" and C_p "per molecule".) Still, the values for $C_p - C_v$ are within the rather wide error margin of the constant A_0.

While the difference between C_p and C_v can be used to explain the curvature in some of the θ_3 *vs.* T curves at high temperature, no reasonable change in A_0 can be found to eliminate the steep drop in θ_3 at low temperature for GeS and the dichalcogenides. Thus, θ_3 cannot be used as an extrapolation for their low temperature heat capacities. Table 1 lists the θ_3 values only for crystals whose heat capacities can be adjusted to yield an approximately constant θ_3 value with reasonable values for A_0.

Two-dimensional Debye functions

The group IV chalcogenides vary in crystal structure from cubic, covalently bonded structures such as SnTe [27] to orthorhombic, layer-type structures of GeS_2 and $GeSe_2$ [28]. The compounds GeS, GeSe and SnS occupy an intermediate position, since they exhibit layer-type structures at low temperatures, but either transform to cubic symmetry (GeSe [29]) or approach a more isotropic structure (GeS [30], SnS [31, 32]) with increasing temperature. For the series of compounds, GeS, GeSe, SnS and SnSe, X-ray diffraction studies [32] have shown that the degree of anisotropic character decreases in the following order

$$GeS \approx GeSe > SnS \approx SnSe \gg GeTe > SnTe.$$

It is apparent that only C_p of the more isotropic compounds can be approximated by the three-dimensional Debye function.

A comparison can now be made between the layer-type structures of some group IV–VI compounds and graphite. The orthorhombic studies of some monochalcogenides (GeS, GeSe, SnS, SnSe) consist of sets of double-layers with strong primary bonding within the double-layers and weak, secondary bonding between adjacent sets of double layers [27, 29, 32]. A more detailed discussion of the structures of the above monochalcogenides is found elsewhere [32]. The dichalcogenides exhibit either an orthorhombic double-layer structure (GeS_2 and $GeSe_2$) [28] or a hexagonal CdI_2-type structure (SnS_2 and $SnSe_2$) [32] composed of sets of triple-layers. With respect to the layer-type structure of graphite, the heat capacity of the layer-type IV–VI compounds could be expected to show a similar behaviour.

The heat capacity of graphite cannot be approximated by standard Debye theory, and as early as 1911 Nernst [35] suggested two "Einstein temperatures"

instead of a single characteristic temperature to be used. Tarasov [4] suggested a two-dimensional Debye function to describe the heat capacity behavior of graphite. This method was modified by several authors [6, 36], culminating in the extension of the Debye theory by Krumhansl and coworkers [8]. Simply stated, the lattice vibrations were divided into the transverse and longitudinal vibrations. Because of the strong anisotropy of graphite the transverse vibrations are expected to be of higher frequency. The overall expression for heat capacity is thus

$$C_v = R\left[D_2\left(\frac{\theta_2(t)}{T}\right) + 2D_2\left(\frac{\theta_2(l)}{T}\right)\right], \tag{6}$$

where $D_2(\theta_2/T)$ is the two-dimensional Debye function

$$D_2\left(\frac{\theta_2}{T}\right) = 2\left(\frac{T}{\theta_2}\right)^2 \int_0^{\Theta_2/T} \frac{x^3 e^x}{(e^x - 1)^2}\, dx \tag{7}$$

Besides for graphite and boron nitride, D_2 fits have been attempted to interpret heat capacities of some layered organocopper compounds [37]. Measured graphite heat capacities (C_p) can be fitted to this combination D_2 function from 0–1000 K, partially due to the small difference between C_p and C_v for graphite. In attempting to fit group IV chalcogenides to Eq. 7, C_v values calculated by the Nernst–Lindemann approximation were used. New tables were generated for θ_2/T from 0.00 to 17.50 in increments of 0.01. These are shown in the appendix. The resulting values of $\theta_2(l)$ and $\theta_2(t)$ for the layer-type crystals of the group IV chalcogenides are shown in Table 1. All listed θ_2-temperatures yielded C_v values in the temperature range 50–250 K within ±3%. Note that while θ_3 is fairly constant with temperature for GeSe and SnS, the C_v data for these compounds

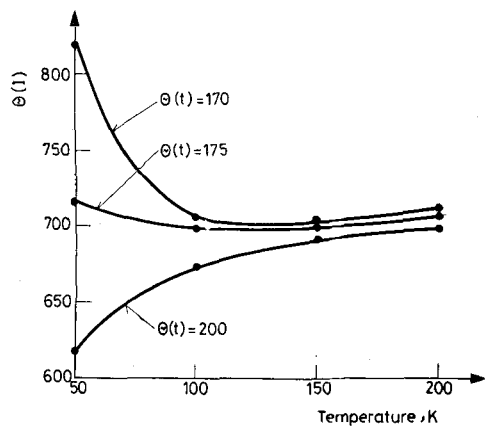

Fig. 7. The variation of $\theta_2(t)$ with temperature for a given $\theta_2(l)$ for GeS_2

can still be fitted to the two-dimensional expression with good results. Other compounds (such as GeTe) cannot be fitted to the two-dimensional form with any degree of agreement. For these only θ_3 data were listed in Table 1. Figure 7 shows the effect of choosing different values of $\theta_2(t)$ for GeS_2. It is apparent that within narrow limits the θ_2 temperatures are fixed.

Discussion

Considering only the measured heat capacities of group IV–VI compounds, it was possible to decide on a three- or two-dimensional Debye function fit. In this discussion it is attempted to correlate the two-dimensional Debye constants with the actual crystal structure of these compounds.

Raman and infrared spectroscopy [38–43] have been used to determine the relative strength of intralayer and interlayer bonding in group IV monochalcogenides and other layered compounds. Using the ratio of intralayer to interlayer force constants as a measure of anisotropy of the crystal structure, the degree of anisotropy is estimated to decrease in the following order [38, 39, 41],

$$GeSe \gtrsim GeS > SnS \gtrsim SnSe\,. \tag{8}$$

The overall trend of decreasing anisotropy is in agreement with that based on the consideration of structural data (Eq. 5) [33]. The above trend (Eq. 8) is consistent with the data in Table 1, which show that $\theta_2(l)$ for all two-dimensional fits is greater than $\theta_2(t)$. Since θ_2 is related to vibrations within the solid by the expression

$$\theta_2(l, t) = \nu(l, t)h/k\,, \tag{9}$$

the greater $\theta_2(l)$ indicates a larger intralayer frequency (thus larger force constant) relative to the interlayer frequency ($\theta_2(t)$).

SnS_2 and $SnSe_2$ are even more layer-like, with estimates of the force constant ratio being of the order of 100 [42]. Spectroscopic data for GeS_2 and $GeSe_2$ are not available, but using their structure for an estimate, the force constant ratio of these compounds would probably be between that of SnS_2 and of the monochalcogenides.

Thus, all heat capacities which could be fitted to a two-dimensional Debye function exhibit layer-type structures, and the relative values of $\theta_2(l)$ and $\theta_2(t)$ are in agreement with the expected values for layer-type structures. Unfortunately, a more quantitative comparison of observed spectroscopic vibrations to $\theta_2(l)$ and $\theta_2(t)$ is prohibited due to a lack of such data for GeS_2 and $GeSe_2$ and due to orientation dependencies of spectroscopic vibrations. However, the evidence presented suggests that the two-dimensional solutions are related to the vibrational modes of these IV–VI compounds.

The authors would like to acknowledge the help of Professor H. H. Hollinger and Professor M. S. Krishnamoorty with the solution of the two-dimensional Debye function. The authors would also like to acknowledge the support of this work in part by the National Aeronautics and Space Administration and by the National Science Foundation, Polymer Programs, Contract No. DMR 78-15279.

References

1. P. DEBYE, Ann. Physik, 39 (1912) 789.
2. A. EUCKEN, Handbuch der Experimentalphysik, VIII (I), Ch. 5, 1929.
3. E. SCHRÖDINGER, Handbuch der Experimentalphysik, X 1926, p. 275.
4. V. V. TARASOV, Compt. Rend. Acad. Sci. URSS, 46 (1945) 110; ibid. 54 (1946) 795; Zh. Fiz. Khim., 24 (1950) 111; ibid. 27 (1953) 1430; Dokl. Akad. Nauk SSSR, 100 (1955) 307.
5. V. V. TARASOV and G. A. YUNITSKII, Zh. Fiz. Khim, 39 (1965) 2077.
6. R. W. GURNEY, Phys. Rev., 88 (1952) 465.
7. B. WUNDERLICH and H. BAUR, Adv. Poly. Sci., 7 (1970) 151.
8. J. A. KRUMHANSL and H. BROOKS, J. Chem. Phys., 21 (1953) 1663; J. C. BOWMAN and J. A. KRUMHANSL, J. Phys. Chem. Sol., 6 (1958) 367.
9. LANDOLT-BÖRNSTEIN, Physikalisch Chemische Tabellen, Springer-Verlag, Berlin, 1961, Ed. 6, Vol. 2, Part 4, p. 736; J. A. BEATTY, J. Math. Phys. (MIT), 6 (1926/27) 1.
10. B. WUNDERLICH, J. Chem. Phys., 37 (1962) 1207.
11. A widely spaced table is given by V. V. TARASOV, New Glass Physics Experiments, Gosstroizdat, Moscow, 1959.
12. H. WIEDEMEIER and F. J. CSILLAG, J. Crystal Growth, 46 (1979) 189.
13. H. WIEDEMEIER and G. PULTZ, to be published.
14. K. C. MILLS, Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides, Butterworths, London, 1974.
15. O. KUBACHEWSKI, E. L. EVANS and C. B. ALCOCK, Metallurgical Thermochemistry, Pergamon, Oxford, 1967.
16. V. M. ZHDANOV, Russ. J. Phys. Chem., 43 (1969) 1468.
17. H. WIEDERMEIER, P. SIEMERS, U. GAUR and B. WUNDERLICH, Thermochim. Acta, 27 (1978) 228.
18. V. M. ZHDANOV, Russ. J. Phys. Chem., 45 (1971) 1357.
19. D. H. PARKINSON and J. E. QUARRINGTON, Proc. Phys. Soc., 67 (1954) 569.
20. A. J. BEVOLO, H. R. SHANKS and D. E. ECKELS, Phys. Rev. B, 13 (1976) 3523.
21. H. WIEDEMEIER, G. PULTZ, U. GAUR and B. WUNDERLICH, Thermochim. Acta, in press.
22. W. W. WELLER and K. K. KELLEY, U. S. Bur. Mines Rept. Invest. (1964) 6511.
23. E. G. KING and S. S. TODD, J. Amer. Chem. Soc., 75 (1953) 3023.
24. V. V. TARASOV, V. M. ZHDANOV and A. K. MALTSEV, Russ J. Phys. Chem., 42 (1968) 685.
25. W. NERNST and F. A. LINDEMANN, Z. Elecktrochem., 17 (1911) 817.
26. N. G. ALIEV, I. G. KERIMOV, M. M. KURBANOV and T. A. MANEDOV, Soviet Phys. Sol. State, 14 (1972) 1304.
27. Semiconducting II—VI, IV—VI and V—VI Compounds, Plenum, New York, 1969.
28. J. BURGEAT, G. LEROUX and A. BRENAC, J. Appl. Cryst., 8 (1975) 325.
29. H. WIEDEMEIER and P. A. SIEMERS, Z. Anorg. Allgem. Chem., 411 (1975) 90.
30. H. WIEDEMEIER and P. A. SIEMERS, Z. Anorg. Allgem. Chem., 431 (1977) 299.
31. H. G. VON SCHNERING and H. WIEDEMEIER, Z. Krist., in press.
32. H. WIEDEMEIER and F. J. CSILLAG, Z. Krist., 149 (1979) 17.
33. H. WIEDEMEIER and H. G. VON SCHNERING, Z. Krist., 148 (1978) 295.
34. F. A. S. AL-ALAMY, A. A. BALCHIN and M. WHITE, J. Mat. Sci., 12 (1977) 2037.

35. W. NERNST, Ann. Physik, 36 (1911) 395.
36. K. KOMATSU and T. NAGAMIYA, J. Phys. Soc. Japan, 6 (1951) 438.
37. P. BLOEMBERGEN and A. R. MIEDEMA, Physica, 75 (1974) 205.
38. H. R. CHANDRASEKHAR, R. G. HUMPHREYS, U. ZWICK and M. CORDONA, Phys. Rev. B., 15 (1977) 2177.
39. P. M. NIKOLIC, L. MILJKOVIC, P. MIHAJLOVIC and B. LAURENCIC, J. Phys. C.: Sol. St. Phys., 10 (1977) L289.
40. D. G. MEAD and J. C. IRWIN, Sol. State Commun., 20 (1976) 885.
41. H. R. CHANDRASEKHAR and U. ZWICK, Sol. State Commun., 18 (1976) 1509.
42. J. L. VEBLE and T. J. WIETLING, Sol. State Commun., 11 (1972) 941.
43. J. D. WILEY, W. J. BUKEL and R. L. SCHMIDT, Phys. Rev. B., 13 (1976) 2489.

RÉSUMÉ — On a examiné les capacités calorifiques à basses températures de 13 chalcogénure du groupe IV. Les capacités calorifiques des cristaux de structures principalement isotrope (GeTe, SnSe, SnTe, PbS, PbSe, PbTe) peuvent être représentées à $\pm 3\%$, par une fonction Debye à trois dimensions ($\theta_3 = 205$, 230, 175, 225, 150 et 130 respectivement). Les capacités calorifiques des cristaux à structures anisotropes (GeS, GeSe, SnS, GeS_2, $GeSe_2$ et SnS_2) ne peuvent être représentées que par des paires de fonctions Debye à deux dimensions, pour les vibrations du réseau longitudinales et transversales (erreur de $\pm 0{,}5$ à 3%; $\theta_2(l) = 505$, 345, 400, 705, 480 et 570, et $\theta_2(t) = 200{,}185$, 160, 175, 100 et 265).

Comme il n'existe pas de tableaux détaillés pour la fonction Debye à deux dimensions les auteurs donnent en appendice un tableau à cinq positions. Des données Raman et infrarouges sont fournies à l'appui de cette analyse.

ZUSAMMENFASSUNG — Die Wärmekapazität bei niedrigen Temperaturen wurde für 13 Chalcogenide der Gruppe IV untersucht. Die Wärmekapazität der Kristalle von hauptsächlich istotroper Struktur (GeTe, SnSe, SnTe, PbS, PbSe, PbTe) kann innerhalb von $\pm 3\%$ durch eine. dreidimensionale Debye-Funktion dargestellt werden ($\theta_3 = 205$, 230, 175, 225, 150 bzw. 130). Die Wärmekapazität von Kristallen anisotroper Struktur (GeS, GeSe, SnS, GeS_2, $GeSe_2$ und SnS_2) konnte für longitudinale und transversale Gittervibrationen nur durch Paare zweidimensionaler Debye-Funktionen dargestellt werden (Fehler: $\pm 0{,}5$ bis 3%; $\theta_2(l) = 505$, 345 400, 705, 480 bzw. 570 und $\theta_2(t) = 200$, 185, 160, 175, 100 bzw. 265).

Da die zweidimensionale Debye-Funktion nicht in allen Einzelheiten tabellarisiert worden ist, wird im Anhang eine fünfstellige Tafel dafür gegeben. Raman- und Infrarot-Angaben bestätigen diese Analyse.

Резюме — Исследованы низкотемпературные теплоемкости 13 халькогенидов группы IV. Теплоемкость кристаллов большой изотропной структуры (GeTe, SnSe, SnTe, PbS, PbSe, PbTe) может быть представлена с ошибкой $\pm 3\%$ трехразмерной дебаевской функцией ($\theta_3 = 205$, 230, 175, 225, 150 и 130, соответственно). Теплоемкость кристаллов с анизотропной структурой (GeS, GeSe, SnS, GeS_2, $GeSe_2$, и SnS_2) может быть представлена только парой двухразмерных дебаевских функций для продольных и поперечных колебаний решетки (ошибка от ± 0.5 до 3%; θ_2 (прод.) = 505, 345, 400, 705, 480 и 570 для соответствующих соединений, а θ_2 (поп.) = 200, 185, 160, 175, 100 и 265). Поскольку двухразмерная дебаевская функция детально ранее не была приведена, авторы приводят ее в приложении. ИК спектры и спектры комбинационного рассеяния подтверждают проведенный анализ теплоемкостей.

Appendix

The following table (Table 2) of $C_v/3R$ as a function of θ_2/T as given by the two-dimensional Debye function was calculated using Eq. 7 of the text. The computer program was based on "Simpson Rule" which states that by breaking the range of the definite integral ($a \leq x \leq b$) into $2n$ intervals of length $h = (b - a)/2n$, then approximately,

$$\int_a^b f(x)\mathrm{d}x = \frac{h}{3}[f(x_0) + 4f(x_1) + 2f(x_2) + 4f(x_3) + \ldots + 2f(x_{2n-2} + 4f(x_{2n-1} + f(x_{2n})] \,. \quad (1a)$$

The number of intervals was chosen to be 100, which leads to an error of less than $+0.000001$ over the whole range of θ_2/T. Above $\theta_2/T = 17.50$ the two dimensional Debye function is represented to better than $\pm 0.02\%$ by the low temperature approximation:

$$D_2(\theta/T) = 14.42468/(\theta/T)^2 \quad (2a)$$

Table 2

Two-dimensional Debye function

Theta/T	Two-dimensional Debye function $C_V/3R$									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.00	1.00000	0.99999	0.99997	0.99995	0.99993	0.99989	0.99985	0.99979	0.99973	0.99966
0.10	0.99958	0.99949	0.99939	0.99929	0.99918	0.99906	0.99893	0.99879	0.99864	0.99849
0.20	0.99833	0.99816	0.99798	0.99779	0.99760	0.99739	0.99718	0.99696	0.99673	0.99650
0.30	0.99625	0.99600	0.99574	0.99547	0.99519	0.99491	0.99462	0,99431	0,99400	0,99369
0.40	0.99336	0.99303	0.99268	0.99234	0.99198	0.99161	0.99124	0.99086	0.99046	0.99007
0.50	0.98966	0.98925	0.98883	0.98840	0.98796	0.98752	0.98706	0.98660	0.98613	0.98566
0.60	0.98517	0.98468	0.98418	0.98367	0.98316	0.98263	0.98210	0.98157	0.98102	0.98047
0.70	0.97991	0.97934	0.97876	0.97818	0.97759	0.97699	0.97638	0.97577	0.97515	0.97452
0.80	0.97389	0.97324	0.97259	9.97194	0.97127	0.97060	0.96992	0.96924	0.96854	0.96784
0.90	0.96713	0.96642	0.96570	0.96497	0.96424	0.96349	0.96274	0.96199	0.96122	0.96045
1.00	0.95968	0.95889	0.95810	0.95731	0.95650	0.95569	0.95488	0.95405	0.95322	0.95239
1.10	0.95154	0.95069	0.94984	0.94897	0.94810	0.94723	0.94635	0.94546	0.94456	0.94366
1.20	0.94276	0.94184	0.94093	0.94000	0.93907	0.93813	0.93719	0.93624	0.93528	0.93432
1.30	0.93336	0.93238	0.93140	0.93042	0.92943	0.92843	0.92743	0.92643	0.92541	0.92439
1.40	0.92337	0.92234	0.92131	0.92027	0.91922	0.91817	0.91711	0.91605	0.91499	0.91391
1.50	0.91283	0.91175	0.91067	0.90957	0.90847	0.90737	0.90626	0.90515	0.90404	0.90291
1.60	0.90178	0.90065	0.89952	0.89838	0.89723	0.89608	0.89492	0.89376	0.89260	0.89143
1.70	0.89026	0.88908	0.88790	0.88671	0.88552	0.88433	0.88313	0.88192	0.88072	0.87950
1.80	0.87829	0.87707	0.87584	0.87462	0.87339	0.87215	0.87091	0.86967	0.86842	0.86717
1.90	0.86592	0.86466	0.86340	0.86213	0.86086	0.85959	0.85831	0.85703	0.85575	0.85447
2.00	0.85317	0.85188	0.85058	0.84929	0.84798	0.84668	0.84537	0.84406	0.84274	0.84142
2.10	0.84010	0.83878	0.83745	0.83612	0.83479	0.83346	0.83212	0.83078	0.82944	0.82809
2.20	0.82674	0.82539	0.82404	0.82268	0.82132	0.81996	0.81860	0.81723	0.81586	0.81449
2.30	0.81312	0.81175	0.81037	0.80899	0.80761	0.80622	0.80484	0.80345	0.80206	0.80067
2.40	0.79928	0.79788	0.79649	0.79509	0.79369	0.79229	0.79088	0.78948	0.78807	0.78666
2.50	0.78525	0.78384	0.78243	0.78101	0.77960	0.77818	0.77676	0.77534	0.77392	0.77249
2.60	0.77107	0.76965	0.76822	0.76679	0.76536	0.76393	0.76250	0.76107	0.75964	0.75821
2.70	0.75677	0.75534	0.75390	0.75246	0.75103	0.74959	0.74815	0.74671	0.74527	0.74383
2.80	0.74238	0.74094	0.73950	0.73806	0.73661	0.73517	0.73372	0.73228	0.73083	0.72939

Two-dimensional Debye function

Theta/T	Two-dimensional Debye function $C_V/3R$									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
2.90	0.72794	0.72649	0.72504	0.72360	0.72215	0.72070	0.71926	0.71781	0.71636	0.71491
3.00	0.71346	0.71201	0.71057	0.70912	0.70767	0.70622	0.70478	0.70333	0.70188	0.70043
3.10	0.69899	0.69754	0.69609	0.69465	0.69320	0.69176	0.69031	0.68887	0.68742	0.68598
3.20	0.68454	0.68309	0.68165	0.68021	0.67877	0.67733	0.67589	0.67445	0.67301	0.67157
3.30	0.67013	0.66870	0.66726	0.66582	0.66439	0.66296	0.66152	0.66009	0.65866	0.65723
3.40	0.65580	0.65437	0.65294	0.65152	0.65009	0.64867	0.64725	0.64582	0.64440	0.64298
3.50	0.64156	0.64014	0.63873	0.63731	0.63590	0.63448	0.63307	0.63166	0.63025	0.62884
3.60	0.62743	0.62603	0.62462	0.62322	0.62182	0.62042	0.61902	0.61762	0.61623	0.61483
3.70	0.61344	0.61205	0.61066	0.60927	0.60788	0.60650	0.60511	0.60373	0.60235	0.60097
3.80	0.59959	0.59821	0.59684	0.59547	0.59410	0.59273	0.59136	0.58999	0.58863	0.58727
3.90	0.58591	0.58455	0.58319	0.58183	0.58048	0.57913	0.57778	0.57643	0.57509	0.57374
4.00	0.57240	0.57106	0.56972	0.56838	0.56705	0.56571	0.56438	0.56305	0.56173	0.56040
4.10	0.55908	0.55776	0.55644	0.55512	0.55381	0.55250	0.55118	0.54988	0.54857	0.54726
4.20	0.54596	0.54466	0.54336	0.54206	0.54077	0.53948	0.53819	0.53690	0.53562	0.53433
4.30	0.53305	0.53177	0.53050	0.52922	0.52795	0.52668	0.52541	0.52414	0.52288	0.52162
4.40	0.52036	0.51910	0.51785	0.51660	0.51535	0.51410	0.51286	0.51161	0.51037	0.50913
4.50	0.50790	0.50666	0.50543	0.50420	0.50298	0.50175	0.50053	0.49931	0.49809	0.49688
4.60	0.49566	0.49445	0.49325	0.49204	0.49084	0.48964	0.48844	0.48724	0.48605	0.48486
4.70	0.48367	0.48248	0.48130	0.48012	0.47894	0.47776	0.47659	0.47542	0.47425	0.47308
4.80	0.47192	0.47075	0.46960	0.46844	0.46728	0.46613	0.46498	0.46383	0.46269	0.46155
4.90	0.46041	0.45927	0.45814	0.45700	0.45587	0.45475	0.45362	0.45250	0.45138	0.45026
5.00	0.44915	0.44804	0.44692	0.44582	0.44471	0.44361	0.44251	0.44141	0.44032	0.43923
5.10	0.43814	0.43705	0.43596	0.43488	0.43380	0.43273	0.43165	0.43058	0.42951	0.42844
5.20	0.42737	0.42631	0.42525	0.42420	0.42314	0.42209	0.42104	0.41999	0.41895	0.41790
5.30	0.41686	0.41583	0.41479	0.41376	0.41273	0.41170	0.41068	0.40965	0.40863	0.40762
5.40	0.40660	0.40559	0.40458	0.40357	0.40257	0.40156	0.40056	0.39957	0.39857	0.39758
5.50	0.39659	0.39560	0.39462	0.39363	0.39265	0.39168	0.39070	0.38973	0.38876	0.38779
5.60	0.38682	0.38586	0.38490	0.38394	0.38299	0.38203	0.38108	0.38013	0.37919	0.37824
5.70	0.37730	0.37636	0.37543	0.37449	0.37356	0.37263	0.37171	0.37078	0.36986	0.36894

5.80	0.36802	0.36711	0.36620	0.36529	0.36438	0.36348	0.36257	0.36167	0.36078	0.35988
5.90	0.35899	0.35810	0.35721	0.35632	0.35544	0.35456	0.35368	0.35280	0.35193	0.35106
6.00	0.35019	0.34932	0.34845	0.34759	0.34673	0.34587	0.34502	0.34417	0.34331	0.34247
6.10	0.34162	0.34077	0.33993	0.33909	0.33826	0.33742	0.33659	0.33576	0.33493	0.33410
6.20	0.33328	0.33246	0.33164	0.33082	0.33001	0.32920	0.32839	0.32759	0.32677	0.32597
6.30	0.32517	0.32437	0.32357	0.32278	0.32199	0.32120	0.32041	0.31962	0.31884	0.31806
6.40	0.31728	0.31650	0.31573	0.31495	0.31418	0.31341	0.31265	0.31188	0.31112	0.31036
6.50	0.30961	0.30885	0.30810	0.30735	0.30660	0.30585	0.30510	0.30436	0.30362	0.30288
6.60	0.30215	0.30141	0.30068	0.29995	0.29922	0.29849	0.29777	0.29705	0.29633	0.29561
6.70	0.29489	0.29418	0.29347	0.29276	0.29205	0.29134	0.29064	0.28994	0.28924	0.28854
6.80	0.28784	0.28715	7.28646	0.28577	0.28508	0.28440	0.28371	0.28303	0.28235	0.28167
6.90	0.28100	0.28032	0.27965	0.27898	0.27831	0.27764	0.27698	0.27632	0.27566	0.27500
7.00	0.27434	0.27369	0.27303	0.27238	0.27173	0.27108	0.27044	0.26980	0.26915	0.26851
7.10	0.26788	0.26724	0.26660	0.26597	0.26534	0.26471	0.26409	0.26346	0.26284	0.26221
7.20	0.26159	0.26098	0.26036	0.25975	0.25913	0.25852	0.25791	0.25731	0.25670	0.25610
7.30	0.25549	0.25489	0.25429	0.25370	0.25310	0.25251	0.25192	0.25133	0.25074	0.25015
7.40	0.24957	0.24899	0.24840	0.24782	0.24725	0.24667	0.24610	0.24552	0.24495	0.24432
7.50	0.24381	0.24325	0.24268	0.24212	0.24156	0.24100	0.24044	0.23989	0.23933	0.23878
7.60	0.23823	0.23767	0.23713	0.23658	0.23603	0.23549	0.23495	0.23441	0.23387	0.23333
7.70	0.23280	0.23226	0.23173	0.23120	0.23067	0.23014	0.22962	0.22909	0.22857	0.22805
7.80	0.22753	0.22701	0.22649	0.22597	0.22546	0.22495	0.22444	0.22393	0.22342	0.22291
7.90	0.22241	0.22190	0.22140	0.22090	0.22040	0.21990	0.21941	0.21891	0.21842	0.21793
8.00	0.21744	0.21695	0.21646	0.21597	0.21549	0.21501	0.21452	0.21404	0.21356	0.21309
8.10	0.21261	0.21213	0.21166	0.21119	0.21072	0.21025	0.20978	0.20931	0.20885	0.20838
8.20	0.20792	0.20746	0.20700	0.20654	0.20608	0.20563	0.20517	0.20472	0.20427	0.20382
8.30	0.20337	0.20292	0.20247	0.20203	0.20158	0.20114	0.20070	0.20026	0.19982	0.19938
8.40	0.19894	0.19851	0.19807	0.19764	0.19721	0.19678	0.19635	0.19592	0.19550	0.19507
8.50	0.19465	0.19422	0.19380	0.19338	0.19296	0.19255	0.19213	0.19171	0.19130	0.19089
8.60	0.19047	0.19006	0.18965	0.18925	0.18884	0.18843	0.18803	0.18762	0.18722	0.18682
8.70	0.18642	0.18602	0.18562	0.18523	0.18483	0.18444	0.18404	0.18365	0.18326	0.18287
8.80	0.18248	0.18209	0.18171	0.18132	0.18094	0.18056	0.18017	0.17979	0.17941	0.17903
8.90	0.17866	0.17828	0.17790	0.17743	0.17716	0.17678	0.17641	0.17604	0.17567	0.17530
9.00	0.17494	0.17457	0.17421	0.17384	0.17348	0.17312	0.17276	0.17240	0.17204	0.17168
9.10	0.17132	0.17097	0.17061	0.17026	0.16991	0.16956	0.16920	0.16886	0.16851	0.16816

Two-dimensional Debye function

Theta/T	Two-dimensional Debye function C_V $3R$									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
9.20	0.16781	0.16747	0.16712	0.16678	0.16644	0.16609	0.16575	0.16541	0.16507	0.16474
9.30	0.16440	0.16406	0.16373	0.16339	0.16306	0.16273	0.16240	0.16207	0.16174	0.16141
9.40	0.16108	0.16075	0.16043	0.16010	0.15978	0.15946	0.15913	0.15881	0.15849	0.15817
9.50	0.15785	0.15754	0.15722	0.15690	0.15659	0.15627	0.15596	0.15565	0.15534	0.15503
9.60	0.15472	0.15441	0.15410	0.15379	0.15349	0.15318	0.15288	0.15257	0.15227	0.15197
9.70	0.15167	0.15137	0.15107	0.15077	0.15047	0.15017	0.14988	0.14958	0.14929	0.14899
9.80	0.14870	0.14841	0.14812	0.14783	0.14754	0.14725	0.14696	0.14667	0.14638	0.14610
9.90	0.14581	0.14553	0.14525	0.14496	0.14468	0.14440	0.14412	0.14384	0.14356	0.14328
10.00	0.14301	0.14273	0.14245	0.14218	0.14190	0.14163	0.14136	0.14109	0.14081	0.14054
10.10	0.14027	0.14001	0.13974	0.13947	0.13920	0.13894	0.13867	0.13841	0.13814	0.13788
10.20	0.13762	0.13735	0.13709	0.13683	0.13657	0.13631	0.13606	0.13580	0.13554	0.13528
10.30	0.13503	0.13477	0.13452	0.13427	0.13401	0.13376	0.13351	0.13326	0.13301	0.13276
10.40	0.13251	0.13226	0.13201	0.13177	0.13152	0.13127	0.13103	0.13079	0.13054	0.13030
10.50	0.13006	0.12982	0.12958	0.12933	0.12910	0.12886	0.12862	0.12848	0.12814	0.12791
10.60	0.12767	0.12743	0.12720	0.12697	0.12673	0.12650	0.12627	0.12604	0.12581	0.12558
10.70	0.12534	0.12512	0.12489	0.12466	0.12443	0.12421	0.12398	0.12375	0.12353	0.12330
10.80	0.12308	0.12286	0.12263	0.12241	0.12219	0.12197	0.12175	0.12153	0.12131	0.12109
10.90	0.12087	0.12066	0.12044	0.12022	0.12001	0.11979	0.11958	0.11936	0.11915	0.11894
11.00	0.11872	0.11851	0.11830	0.11809	0.11788	0.11767	0.11746	0.11725	0.11704	0.11684
11.10	0.11663	0.11642	0.11622	0.11601	0.11581	0.11560	0.11540	0.11520	0.11499	0.11479
11.20	0.11459	0.11439	0.11419	0.11399	0.11379	0.11359	0.11339	0.11319	0.11299	0.11279
11.30	0.11260	0.11240	0.11221	0.11201	0.11182	0.11162	0.11143	0.11123	0.11104	0.11085
11.40	0.11066	0.11047	0.11028	0.11009	0.10990	0.10971	0.10952	0.10933	0.10914	0.10895
11.50	0.10877	0.10858	0.10839	0.10821	0.10802	0.10784	0.10765	0.10747	0.10729	0.10710
11.60	0.10692	0.10674	0.10656	0.10638	0.10620	0.10602	0.10584	0.10566	0.11548	0.10530
11.70	0.10512	0.10494	0.10477	0.10459	0.10441	0.10424	0.10406	0.10389	0.10371	0.10354
11.80	0.10337	0.10319	0.10302	0.10285	0.10267	0.10250	0.10233	0.10216	0.10199	0.10182
11.90	0.10165	0.10148	0.10131	0.10115	0.10098	0.10081	0.10061	0.10048	0.10031	0.10015
12.00	0.09998	0.09982	0.09965	0.09949	0.09932	0.09916	0.09900	0.09883	0.09867	0.09851

12.10	0.09835	0.09819	0.09803	0.09787	0.09771	0.09755	0.09739	0.09723	0.09707	0.09691
12.20	0.09676	0.09660	0.09644	0.09628	0.09613	0.09597	0.09582	0.09566	0.09551	0.09535
12.30	0.09520	0.09505	0.09489	0.09474	0.09459	0.09444	0.09428	0.09413	0.09398	0.09383
12.40	0.09368	0.09353	0.09338	0.09323	0.09308	0.09294	0.09279	0.09264	0.09249	0.09235
12.50	0.09220	0.09205	0.09191	0.09176	0.09161	0.09147	0.09132	0.09118	0.09104	0.09089
12.60	0.09075	0.09061	0.09046	0.09032	0.09019	0.09004	0.08990	0.08976	0.08961	70.0894
12.70	0.08933	0.08919	0.08905	0.08892	0.08878	0.08864	0.08850	0.08836	0.08823	0.08809
12.80	0.08795	0.08781	0.08768	0.08754	0.08741	0.08727	0.08714	0.08700	0.08687	0.08673
12.90	0.08660	0.08647	0.08633	0.08620	0.08607	0.08594	0.08580	0.08567	0.08551	0.08541
13.00	0.08528	0.08515	0.08502	0.08489	0.08476	0.08463	0.08450	0.08437	0.08424	0.08411
13.10	0.08399	0.08386	0.08373	0.08361	0.08348	0.08335	0.08323	0.08310	0.08297	0.08285
13.20	0.08272	0.08260	0.08248	0.08235	0.08223	0.08210	0.08198	0.08186	0.08173	0.08161
13.30	0.08149	0.08137	0.08125	0.08112	0.08100	0.08088	0.08076	0.08064	0.08052	0.08040
13.40	0.08028	0.08016	0.08004	0.07993	0.07981	0.07969	0.07957	0.07945	0.07934	0.07922
13.50	0.07910	0.07898	0.07887	0.07875	0.07864	0.07852	0.07840	0.07829	0.07817	0.07806
13.60	0.07795	0.07783	0.07772	0.07760	0.07749	0.07738	0.07726	0.07715	0.07704	0.07693
13.70	0.07681	0.07670	0.07659	0.07648	0.07637	0.07627	0.07615	0.07604	0.07593	0.07582
13.80	0.07571	0.07560	0.07549	0.07538	0.07527	0.07516	0.07506	0.07495	0.07484	0.07473
13.90	0.07463	0.07452	0.07441	0.07431	0.07420	0.07409	0.07399	0.07388	0.07378	0.07367
14.00	0.07357	0.07346	0.07336	0.07325	0.07315	0.07304	0.07294	0.07284	0.07273	0.07263
14.10	0.07263	0.07243	0.07232	0.07222	0.07212	0.07202	0.07192	0.07182	0.07171	0.07161
14.20	0.07151	0.07141	0.07131	0.07121	0.07111	0.07101	0.07091	0.07081	0.07072	0.07062
14.30	0.07052	0.07042	0.07032	0.07022	0.07013	0.07003	0.06993	0.06983	0.06874	0.06964
14.40	0.06954	0.06945	0.06935	0.06925	0.06916	0.06906	0.06897	0.06887	0.06878	0.06868
14.50	0.06859	0.06849	0.06840	0.06831	0.06821	0.06812	0.06803	0.06793	0.06784	0.06775
14.60	0.06765	0.06756	0.06747	0.06738	0.06729	0.06719	0.06710	0.06701	0.06692	0.06683
14.70	0.06674	0.06665	0.06656	0.06647	0.06638	0.06629	0.06620	0.06611	0.06602	0.06593
14.80	0.06584	0.06575	0.06566	0.06557	0.06549	0.06540	0.06531	0.06522	0.06514	0.06505
14.90	0.06496	0.06487	0.06479	0.06470	0.06461	0.06453	0.06444	0.06436	0.06427	0.06418
15.00	0.06410	0.06401	0.06393	0.06384	0.06376	0.06367	0.06359	0.06350	0.06342	0.06334
15.10	0.06325	0.06317	0.06309	0.06300	0.06292	0.06284	0.06275	0.06267	0.06259	0.06251
15.20	0.06242	0.06234	0.06226	0.06218	0.06210	0.06202	0.06193	0.06185	0.06177	0.06169
15.30	0.06161	0.06153	0.06145	0.06137	0.06129	0.06121	0.06113	0.06105	0.06097	0.06089
15.40	0.06081	0.06074	0.06066	0.06058	0.06050	0.06042	0.06034	0.06027	0.06019	0.06011

Two-dimensional Debye function

Theta/T	Two-dimensional Debye function $C_V/3R$									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0-09
15.50	0.06003	0.05996	0.05988	0.05980	0.05972	0.05965	0.05957	0.05949	0.05942	0.05934
15.60	0.05927	0.05919	0.05911	0.05904	0.05896	0.05889	0.05881	0.05874	0.05866	0.05859
15.70	0.05851	0.05844	0.05837	0.05829	0.05822	0.05814	0.05807	0.05800	0.05792	0.05785
15.80	0.05778	0.05770	0.05763	0.05756	0.05749	0.05741	0.05734	0.05727	0.05720	0.05712
15.90	0.05705	0.05698	0.05691	0.05684	0.05677	0.05670	0.05663	0.05655	0.05648	0.05641
16.00	0.05634	0.05627	0.05620	0.05613	0.05606	0.05599	0.05592	0.05585	0.05578	0.05571
16.10	0.05564	0.05558	0.05551	0.05544	0.05537	0.05530	0.05523	0.05516	0.05510	0.05503
16.20	0.05496	0.05489	0.05482	0.05476	0.05469	0.05462	0.05456	0.05449	0.05442	0.05435
16.30	0.05429	0.05422	0.05416	0.05409	0.05402	0.05396	0.05389	0.05383	0.05376	0.75369
16.40	0.05363	0.05356	0.05350	0.05343	0.05337	0.05330	0.05324	0.05317	0.05311	0.05304
16.50	0.05298	0.05292	0.05285	0.05279	0.05272	0.05266	0.05260	0.05253	0.05247	0.05241
16.60	0.05234	0.05228	0.05222	0.05216	0.05209	0.05203	0.05197	0.05191	0.05184	0.05178
16.70	0.05172	0.05166	0.05160	0.05153	0.05147	0.05141	0.05135	0.05129	0.05123	0.05117
16.80	0.05111	0.05104	0.05098	0.05092	0.05086	0.05080	0.05074	0.05068	0.05062	0.05056
16.90	0.05050	0.05044	0.05038	0.05032	0.05026	0.05021	0.05015	0.05009	0.05003	0.04997
17.00	0.04991	0.04985	0.04979	0.04973	0.04968	0.04962	0.04956	0.04950	0.04944	0.04939
17.10	0.04933	0.04927	0.04921	0.04916	0.04910	0.04904	0.04898	0.04893	0.04887	0.04881
17.20	0.04876	0.04870	0.04864	0.04859	0.04853	0.04847	0.04842	0.04836	0.04831	0,04825
17.30	0.04819	0.04814	0.04808	0.04803	0.04797	0.04792	0.04786	0.04781	0.04775	0.04770
17.40	0.04764	0.04759	0.04753	0.04748	0.04742	0.04737	0.04732	0.04726	0.04721	0.04715