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Heat capacity of germanium crystals with various isotopic composition

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Abstract

The heat capacity of three pure ($n, p \leq 2 \times 10^{16} \text{ cm}^{-3}$) germanium crystals with different isotopic compositions was measured in the temperature range from 2.8 K to 100 K. These samples, one made of enriched ^{70}Ge (95.6%), Ge of natural isotopic composition and $n, p < 10^{14} \text{ cm}^{-3}$, and one of the largest possible isotopic mass variance $^{70/76}\text{Ge}$ (43%/48%) with $n, p < 10^{14} \text{ cm}^{-3}$, show a change of the molar heat capacity (and corresponding Debye temperature, θ_D) as expected from the average mass variation, corresponding to $\theta_D \propto M^{-0.5}$ ($M =$ molar mass) at low temperatures. The mass effect is best visible around 21.5 K, at the minimum of the corresponding Debye temperatures θ_D , and amounts to $\Delta\theta_D = 5.3 \text{ K}$ for the difference between the Debye temperatures of ^{70}Ge and $^{70/76}\text{Ge}$. The specific heat capacity of the natural Ge crystal agrees within 2% with the best data available in the literature taken on much larger masses of Ge.

1. Introduction

Most elements are found in nature as a mixture of stable isotopes. The isotopic composition affects many physical properties of solids [1–4], e.g. density, heat conductivity, phonon frequencies as detected by Raman and optical spectroscopy, crystalline electric field effects, superconducting transition temperature, displacive and ferroelectric transition temperatures etc. Isotopic disorder, as an ideal point defect, varies exclusively the atomic mass, i.e. the lattice parameters are not affected primarily. The recent availability of macroscopic quantities of isotopically well defined crystals of diamond, germanium and silicon thus has triggered intensive studies [1, 5]. However, only a few investigations report on the effect of isotopic composition on the thermal properties of solids. Thermal conductivity measurements were performed with ^4He , Ne, C, Si, Ge, LiF and B_4C isotopes (for a short overview see [5]). A recent comprehensive study investigated the influence of varying isotopic compositions on the thermal conductivity of pure Ge

crystals [5]. An isotopically highly enriched (99.99%) ^{70}Ge high-purity crystal [5] and an isotopically strongly enriched (99.86%) ^{28}Si crystal displayed heat conductivities up to an order of magnitude larger than pure natural isotope mixture crystals [6]. Besides studies on helium (^3He , ^4He) and hydrogen (H, D, T) isotopes [7] and their compounds, heat capacity experiments on samples with different isotopic composition have been reported rather scarcely [7–15]. Some superconducting [10] and displacive/ferroelectric [11] phase transitions have been investigated using isotope samples. Of relevance here are experiments on cryocrystals [12], e.g. of N_2 [13] and Ne [14, 15], which, however, are very compressible, have strongly anharmonic interatomic potentials and thus large thermal expansions. For light noble gas solids as neon (^{20}Ne and ^{22}Ne), where the isotope effect is significant, strong quantum effects are present [14, 15]. No specific heat data are available for isotopes of heavier elements, especially not for germanium, although the stable Ge isotopes are ideal for studying isotopic effects for the following reasons.

- (i) Natural Ge is composed of five isotopes with sizeable abundance (^{70}Ge 21.23%, ^{72}Ge 27.66%, ^{73}Ge 7.73%, ^{74}Ge 35.94, ^{76}Ge 7.44% [16]).
- (ii) These stable isotopes span a large range of molar masses between $69.924\,25\text{ g mol}^{-1}$ (^{70}Ge) and $75.921\,40\text{ g mol}^{-1}$ (^{76}Ge) [17].
- (iii) Germanium (like silicon) can be prepared with high elemental purity and in almost perfect crystals.

This paper describes a study of the specific heat capacity of two very pure and one lightly hole-conducting germanium single crystals, with various isotopic composition in the temperature range from 2.8 K to 100 K. The data are compared to the results reported earlier in the literature for pure Ge of natural isotopic mixture [18–25] and to results on crystalline Ne isotopes [14, 15]. The Ge isotope data offer a unique opportunity to display some of the basics of the Debye theory of lattice heat capacity on a ‘model solid’ using the concept of corresponding Debye temperature. In contrast to $c_p(T)$ or $c_v(T)$ data for cryocrystals quantum effects and anharmonicities do not play a role for Ge isotopes. The study also demonstrates the advance of calorimetry towards smaller samples.

2. Specific heat capacity of germanium

The heat capacity of germanium (with natural isotopic composition) has been measured repeatedly [18–25] on large (200 g to 600 g mass) poly- and single-crystalline samples. The results show large differences, especially in the low temperature range ($T < 20\text{ K}$), which only partially results from the different sample purity. [19], [21] and [25] report on the specific heat capacity of ‘pure’ germanium, i.e. samples with a low concentration of uncompensated charge carriers, n , $p < 10^{-15}\text{ cm}^{-3}$ and high resistivities at 300 K. The other samples [18, 20, 22–24] contained relatively large amounts of impurities, as displayed by the high carrier concentration (n , $p = 10^{16}\text{--}10^{19}\text{ cm}^{-3}$) and by the low resistivity ($\rho = 0.5\text{--}13\ \Omega\text{ cm}$ at 300 K).

For general information, figure 1 displays, in a plot of $c_p(T)/T^3$ against T , the molar heat capacity of germanium with natural isotopic composition ($M = 72.61\text{ g mol}^{-1}$) in the temperature range up to 100 K: (i) the present study and (ii) the best available data from literature, being data from [18], [19], [21], [24] and [25], whereby only [21] covers the whole range from liquid helium temperature to room temperature.

For the low temperature region, only Flubacher *et al* [21] (temperature range measured: 2–300 K) and Devyatikh *et al* [25] (2.5–15 K) used well defined high-purity, i.e. high-resistivity, germanium with $\rho = 59\ \Omega\text{ cm}$ and $N < 10^{14}\text{ cm}^{-3}$, and $\rho = 65\ \Omega\text{ cm}$ and $N < 5 \times 10^{10}\text{ cm}^{-3}$ (at 77 K), respectively. The sample studied by Estermann and Weertman [19] (20–200 K) also may be considered as high-purity material; an impurity level of $2.8 \times 10^{14}\text{ cm}^{-3}$

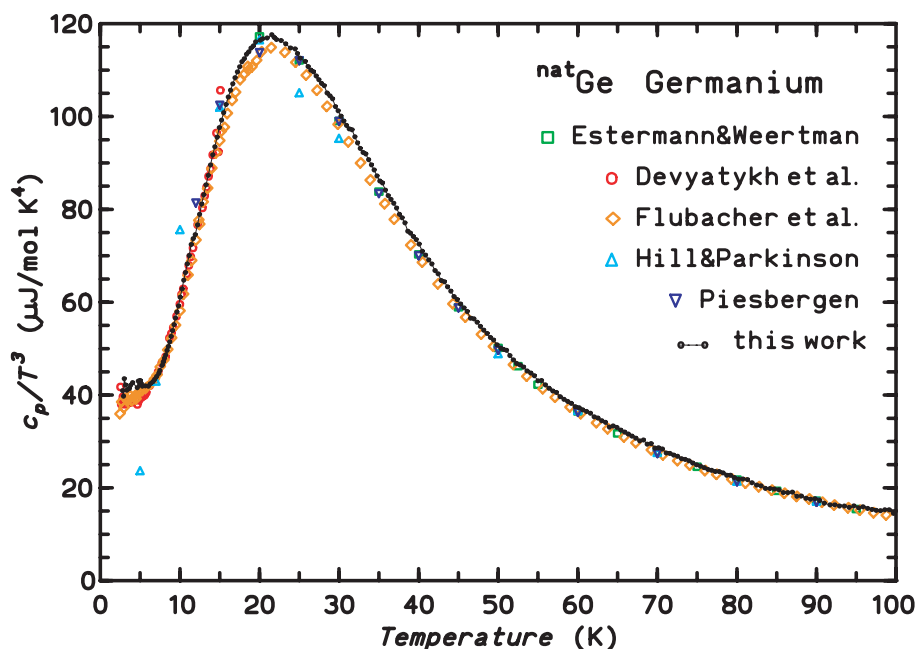


Figure 1. Molar heat capacity c_p/T^3 against T of germanium with a natural isotopic composition of five samples taken from the literature [19, 25, 21, 18, 24] and for the crystal sample ^{nat}Ge measured in this work. The plot symbols (small circles) for the latter data set have been connected by a thin line for clarity.

was indicated. The results of [21] and [25] coincide within 2.5% in the range 2.5–15 K but these results deviate, below 15 K, by up to 15% from the data published by Keesom *et al* [20, 22, 23]. The difference is still larger and amounts to 40% for the results reported by Hill and Parkinson [18] (5–160 K) and by Piesbergen [24] (12–200 K). The published results differ also since the germanium used in early studies contained more and other impurities, i.e. Ga, Si, Sn, Sb and As at the 10^{18} cm^{-3} level [20, 23]. The impurity composition of the samples was not reported except for the sample of [25] that contained atomic fractions of 2×10^{-9} Mn and 3×10^{-7} Si.

For the higher temperatures ($T > 20$ K), the results reported by Flubacher *et al* [21] and Piesbergen [24] differ by not more than 1% in the range 20–200 K, whereas the data given by Hill and Parkinson [18] (5–160 K) and Estermann and Weertman [19] (20–200 K) show larger deviations of about $\pm 1.5\%$.

In [23] the electronic specific heat coefficient γ was accessed for n-type Ge samples. Values of $\gamma \approx 0.02 \text{ mJ mol}^{-1} \text{ K}^{-2}$ were found for samples with $n \approx 10^{18} \text{ cm}^{-3}$ in the temperature range 0.4 K to 4.5 K and for a pure Ge sample $\gamma = 0 \pm 0.001 \text{ mJ mol}^{-1} \text{ K}^{-2}$ was found. In some previous measurements for temperatures below 5 K, the desorption of adsorbed ^4He exchange gas was observed to cause problems (see e.g. [22, 23]).

3. Experimental details

The preparation of the Ge crystal samples has been described elsewhere [3, 26]. The material of the three crystals studied is identical to those for which the heat conductivity was measured recently [5]. The materials are characterized by their molar mass M and their isotopic mass variance g , defined as $g = (\sum c_i M_i^2 - (\sum c_i M_i)^2) / (\sum c_i M_i)^2$. The percentage isotopic

compositions c_i are the following:

^{70}Ge : 95.6 ^{70}Ge , 3.8 ^{72}Ge , 0.6 ^{74}Ge	$M = 70.024 \text{ g mol}^{-1}$	$g = 4.0 \times 10^{-5}$
$^{\text{nat}}\text{Ge}$: 21.23 ^{70}Ge , 27.66 ^{72}Ge , 7.73 ^{73}Ge , 35.94 ^{74}Ge , 7.44 ^{76}Ge	$M = 72.71 \text{ g mol}^{-1}$	$g = 58.7 \times 10^{-5}$
$^{70/76}\text{Ge}$: 43 ^{70}Ge , 2 ^{72}Ge , 7 ^{74}Ge , 48 ^{76}Ge	$M = 73.123 \text{ g mol}^{-1}$	$g = 153 \times 10^{-5}$

Unfortunately, the rod-shaped crystal of ^{70}Ge (99.99%) used for thermal conductivity measurements [5] could not be mounted in the calorimeter due to its length. Instead, we used a sample (^{70}Ge ; labelled ^{70}Ge (95.6%) in [5]) whose material was slightly hole conducting with a concentration $p = 2 \times 10^{16} \text{ cm}^{-3}$. The material for sample $^{70/76}\text{Ge}$ was grown for the purpose of maximizing isotopic disorder (maximum thermal resistance; see [5]). The level of impurities lies below 10^{14} cm^{-3} at room temperature for the $^{\text{nat}}\text{Ge}$ (labelled $^{\text{nat}}\text{Ge}$ 1 in [5]) and $^{70/76}\text{Ge}$ sample material. None of the materials were intentionally doped. The samples used for the heat capacity experiments were two or three rod-shaped pieces of size $\approx 2.5 \times 2.5 \times 10 \text{ mm}^3$, having the total masses 0.3048 g, 1.1362 g and 0.5138 g for ^{70}Ge , $^{\text{nat}}\text{Ge}$ and $^{70/76}\text{Ge}$ samples, respectively. We note that these sample masses are two to three orders of magnitude less than those used in previous studies (cf e.g. [20, 21, 23]).

For the temperature range from 2.8 K to 100 K, a modernized version of an quasi-adiabatic vacuum calorimeter, described in [27] and [28] was utilized. The calorimeter uses the discontinuous step-heating (Nernst) method and high-precision isothermal shield control. The heating steps ΔT were about 1–4% of T or less than 0.6 K so that no curvature correction is necessary. The sample holder consists of a sapphire plate equipped with an electrical heater resistor and a commercially calibrated Ge resistance thermometer (Cryocal). The samples were mounted onto the calorimetric sample holder [29] with a minute amount (2 to 4 mg) of Apiezon N grease. The heat capacity of the sample holder platform, determined in a separate run, and of the grease [30] were subtracted from the total measured heat capacity. The basic instrumental inaccuracy for the present experiments is about 2% between 6 K and 77 K, while the sample-to-sample reproducibility is well within 0.5%. Due to the decreasing sensitivity of the Ge thermometer the data scatter more strongly with increasing temperature and the inaccuracy increases (for $T > 77 \text{ K}$). Below 4.2 K the heat capacity of the two lighter samples was too low to be evaluated with a reasonable error. The inaccuracy increases here with decreasing temperature and is estimated to be $\approx 6\%$ below 4.2 K.

4. Results and discussion

The results of various heat capacity measurements with $^{\text{nat}}\text{Ge}$ (2.46–100 K) are shown in figure 1, as mentioned before. Figure 2 displays the molar heat capacity of the three investigated Ge isotope samples, again in a plot of $c_p(T)/T^3$ against T (figure 2, lower panel), as well as in the representation of the corresponding (equivalent) Debye temperature θ_D as a function of temperature T (figure 2, upper panel), calculated by solving the equation $c_p(T) = 3RD(\theta_D/T)$, where R is the gas constant and D denotes the Debye function [31–33]. Molar heat capacity and Debye temperature show the characteristic low temperature behaviour known from Ge and other solids [21, 32, 33]. Most typical is the strong minimum of $\theta_D(T)$ around 20 K, as typical for diamond structure solids, due to the serious departure from the Debye approximation. Anharmonic effects become important only for $T > \theta_D(0)/3$, where $\theta_D(T)$ saturates and starts to decrease with increasing T [21].

The $c_p(T)$ data for $^{\text{nat}}\text{Ge}$ in the temperature range from 2.8 K to 6.2 K can be fitted by $\gamma T + \beta T^3$. The result is $\gamma = -0.003(5) \text{ mJ mol}^{-1} \text{ K}^{-2}$, i.e. within the statistical error of the

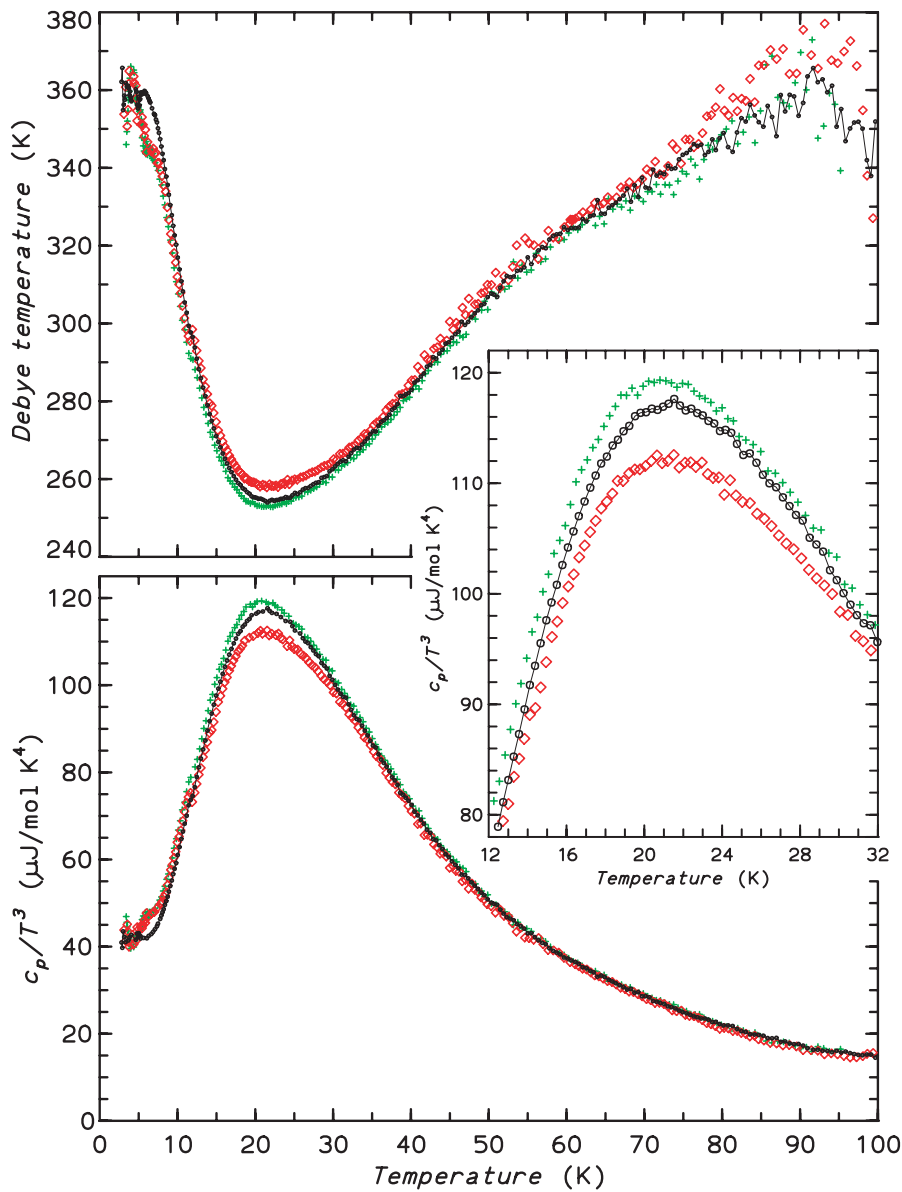


Figure 2. Molar heat capacity $c_p(T)$ of the three measured crystal samples: $^{70/76}\text{Ge}$ (+), $^{\text{nat}}\text{Ge}$ (circles connected by a thin line) and ^{70}Ge (diamonds): plot of c_p/T^3 against T (lower panel), and (upper panel) corresponding Debye temperature θ_D as a function of temperature T . The inset shows a magnification of the plot in the lower panel.

fit, a value for γ as expected for a sample with $p = 2 \times 10^{16} \text{ cm}^{-3}$ (cf the Ge samples in [23]), and $\beta = 0.00423(2) \text{ mJ mol}^{-1} \text{ K}^{-4}$, which corresponds to $\theta_D(0) = 358(3) \text{ K}$ (taking into account the above given inaccuracy). The initial Debye temperature $\theta_D(0)$ is too low compared to previous experimental results (374(2) K [21]; 371.3 K [23]) and to the value derived from elastic constants (374.0 K [23]). This might be due to the desorption of adsorbed gas on the sample/sample holder surfaces, since the calorimeter was cooled down to 20 K with a few

Table 1. Characteristic thermal parameters of the three isotope samples at their minima of the Debye temperature (at T_{\min} ; near 21.5 K) as compared to $^{\text{nat}}\text{Ge}$ and entropy S and enthalpy H at 77 K.

	^{70}Ge	$^{\text{nat}}\text{Ge}$	$^{70/76}\text{Ge}$
M (g mol $^{-1}$)	70.024	72.61	73.123
$(\Delta M/M(\text{nat}))$ (%)	-3.56	0	+0.71
(c_p/T^3) (J mol $^{-1}$ K $^{-4}$)	1.118	1.171	1.194
$(\Delta c_p/c_p(\text{nat}))$ (%)	-4.3	0	+2.0
T_{\min} (K)	21.6	21.8	21.4
$\theta_D(T_{\min})$ (K)	258.2	254.3	252.9
$\Delta\theta_D(T_{\min})$ (K)	+3.9	0	-1.4
$(\Delta\theta_D/\theta_D(\text{nat}))$ (%)	+1.5	0	-0.6
$\theta_D(T_{\min})M^{0.5}$	2161	2167	2163
$M^{3/2}(c_p/T^3)^{-1}$	524	528	524
S (77 K) (J mol $^{-1}$ K $^{-1}$)	6.788	6.894	6.977
H (77 K) (J mol $^{-1}$)	343.3	347.9	351.8

mbar of ^3He exchange gas. In comparison to the presumably most accurate data for $c_p(T)$ of $^{\text{nat}}\text{Ge}$ by Flubacher *et al* with estimated 0.2% inaccuracy [21] our data are about 2% higher in the whole temperature range. However, our discussion will concentrate on temperatures between 10 K and 77 K and we will mainly compare the current isotope data with each other.

The minimum of the corresponding Debye temperature occurs near 21.5 K and is related to the first maximum of the density of states resulting from the lowest acoustic phonon branch. At this special temperature, the isotopic effect is best visualized and we can compare well our experimental data of the isotopes: the molar specific heat of ^{70}Ge is 4.7% higher than that of $^{\text{nat}}\text{Ge}$, but c_p of $^{70/76}\text{Ge}$ is lower by 1.7%, and, vice versa, the corresponding Debye temperatures for ^{70}Ge and $^{70/76}\text{Ge}$ are, 4.5 K higher and 1 K lower, respectively, when compared to $^{\text{nat}}\text{Ge}$. The differences of the thermal parameters of the three isotopes are listed in table 1. At higher temperatures, the isotopic mass effect is still visible. The scatter in the $\theta_D(T)$ data increases with T but it is clearly discernible that θ_D at a given T increases in the order of the samples $^{70/76}\text{Ge}$, $^{\text{nat}}\text{Ge}$ and ^{70}Ge .

According to the Debye isotropic model [31–33], based on harmonic approximation, the Debye temperature θ_D varies as the inverse square root of the isotopic (total) mass of the cell, $\theta_D \propto (\sum(U_{ii}/M)^{0.5})$ at low temperature ($T < \theta_D(0)/10$) for a crystal consisting of one type of atom, where M is the atomic (or molecular) mass and U_{ii} denotes the second derivative of the potential energy of the crystal with respect to the component i of displacement of an atom from its equilibrium position. The molar heat capacity c itself is proportional to \sqrt{M}^3 . Thus for different isotopes of an element (or mixtures of them and also for the respective compounds), the relations $\theta_D\sqrt{M} = \text{const}$ and $cM^{3/2} = \text{const}$ should be valid. These postulates are tested in table 1. The agreement is excellent within the experimental errors (within 0.3% and 0.7%, respectively), and thus demonstrate that variation of the average mass M is the dominant effect determining the heat capacity when the isotopic composition is changed. The influence of the change of lattice distance a is negligible. A comparison with data known for diamond ($^{12}\text{C}/^{13}\text{C}$) shows that, in the case of carbon, a 1% change of atomic mass, ΔM , induces only a variation of lattice distance by $\Delta a/a = 2$ ppm, i.e. nearly 1000 times smaller than the change of specific heat capacity [8, 9]. This means that, within the experimental resolution of precision calorimetric experiments, the lattice parameters can be considered the same for all Ge isotopes. At low temperatures the lattice effect on c_p is significant for isotopes of cryocrystals [12].

Fugate and Swenson [14] demonstrated the constancy of $\theta_D(0)\sqrt{M}$ for solid ^{20}Ne , $^{\text{nat}}\text{Ne}$

and ^{22}Ne isotopes to about 0.8%. Their study, however, was complicated by impurities of their isotope samples and by the necessity of calculating $c_V(T)$ for the ^{22}Ne and a $^{\text{nat}}\text{Ne}$ sample measured under isobaric conditions. In contrast to Ge solid Ne has a large volume expansion (4.4% between 0 K and the triple point [14]). So, in addition, the $\theta_D(T)$ curves had to be corrected for the increase of the molar volume. Somoza and Fenichel [15] performed similar measurements and compared their results with more elaborate theories for cryocrystals. It remains to remark that isotope effects on $c_p(T)$ in molecular cryocrystals can also be connected to rotational modes, as e.g. in N_2 [12, 13].

Calculations for the difference $\Delta c_{\text{isotope}}$ between the values of molar heat capacity of the isotopes show that $\Delta c_{\text{isotope}}$ increases with temperature since $c_p(T)$ increases most strongly for the material with the greatest molar mass. $\Delta c_{\text{isotope}}$ reaches a maximum around $\theta_D(0)/4$ (≈ 90 K for Ge), and at the limit of high temperatures, it approaches zero [13]. Within the resolution and the scatter of our experiments, the difference $\Delta c_{\text{isotope}}$ is seen to increase continuously up to temperatures of 77 K for the case of $^{70/76}\text{Ge}$ compared to $^{\text{nat}}\text{Ge}$, while a negative $\Delta c_{\text{isotope}}$ of about the same absolute size is visible for the difference between ^{70}Ge and $^{\text{nat}}\text{Ge}$.

Figure 2 (inset) indicated a small change of the maximum of c_p in the vicinity of 21.5 K. The maximum occurs slightly (several 0.1 K) lower for $^{70/76}\text{Ge}$ as compared to $^{\text{nat}}\text{Ge}$ and ^{70}Ge . This is approximately consistent with the shift of the first-order Raman spectra found for Ge isotopes [5]. The Raman shift between $^{\text{nat}}\text{Ge}$ and ^{70}Ge amounts to 5 cm^{-1} (304.5 and 309.5 cm^{-1} , respectively) [34], i.e. to a 1.63% line shift, which in the first order approximation corresponds to a similar temperature shift, i.e. $\Delta T = 0.34$ K, in agreement with the experimental result.

The change of average isotopic mass also leads to a change of entropy. At 77 K the experimental entropy S of $^{70/76}\text{Ge}$ is enhanced by $\approx 0.08\text{ J mol}^{-1}\text{ K}^{-1}$; that of ^{70}Ge is lowered by $\approx 0.11\text{ J mol}^{-1}\text{ K}^{-1}$ with respect to the entropy of $^{\text{nat}}\text{Ge}$ ($6.894\text{ J mol}^{-1}\text{ K}^{-1}$). The enthalpy H is 1.1% larger for $^{70/76}\text{Ge}$ and 1.3% lower for ^{70}Ge , respectively, in comparison to $^{\text{nat}}\text{Ge}$ at 77 K.

5. Summary

Though the mass of the enriched Ge isotope crystals was rather low to perform a sufficiently accurate heat capacity measurement, the basis of the Debye theory of lattice heat capacity—the harmonic approximation for lattice vibrations—could be demonstrated for the first time on isotopes of a crystalline solid (not a cryocrystal). The three samples had strongly different variances g of the isotope composition, which had drastic consequences for the thermal conductivity [5]. Within the relative accuracy of our $c_p(T)$ data no deviation from the scaling $\theta_D = \text{const}/\sqrt{M}$ could be detected. The use of the harmonic approximation and of this scaling is trivial and taken for granted by most scientists; however, it could only be demonstrated on materials of different elemental composition and thus of (slightly) different chemical bonding or on compressible cryocrystals. If larger amounts of pure isotopically designed germanium or other pure element crystals become available it would be interesting to check the approximation to a higher accuracy.

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Note added in proof. Recently, the relative lattice parameter differences $\Delta a/a$ for Ge isotope crystals were determined experimentally [35]. For our crystals of ^{70}Ge and $^{70/76}\text{Ge}$ differences $\Delta a/a$ of -27×10^{-6} and -11×10^{-6} at 30 K

and 300 K, respectively, can be inferred. Thus, the lattice effect is larger than estimated on the basis of the diamond ($^{12}\text{C}/^{13}\text{C}$) data but still well below the resolution of calorimetric experiments.

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