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Thermal properties of boron and borides

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The influence of point defects on the thermal conductivity of polycrystalline β-B has been measured from 1 to 1000 K. Above 300 K, samples containing 2 at. % Hf and Zr have thermal conductivities close to that of amorphous boron, indicating very strong phonon scattering. A thermal conductivity of equal magnitude has also been measured near and below room temperature for nearly stoichiometric single crystals of the theoretical composition YB_{68}. On the basis of a comparison with earlier measurements to temperatures as low as 0.1 K, it is concluded that the thermal conductivity of crystalline YB_{68} is indeed very similar, if not identical, to that expected for amorphous boron over the entire temperature range of measurement (0.1–300 K). Measurements of the specific heat of nearly stoichiometric YB_{68} between 1.5 and 30 K also reveal a linear-specific-heat anomaly of the same magnitude as is characteristic for amorphous solids, in fair agreement with earlier measurements by Bilir *et al.* It is concluded that the lattice vibrations of crystalline YB_{68} are glasslike.

INTRODUCTION

The lattice vibrations of boron and boron-rich borides, and the heat transport by these vibrations, confront the solid-state scientist with an amazing variety of fascinating questions which can be explored through measurements of specific heat and thermal conductivity. Some of these studies have been reviewed recently.[1,2] In this paper, we will report measurements of the thermal conductivity of doped β-boron. We will be particularly concerned with the question of minimum thermal conductivity, i.e., the lowest conductivity that can be achieved for these solids.[3] To answer this question, it will be useful to also consider the thermal conductivity and specific heat of nearly stoichiometric borides with the crystal structure of YB_{68}, and we report measurements of thermal conductivity and specific heat for these substances. We will begin by summarizing information on the samples studied and experimental methods used.

EXPERIMENTAL MATTERS

The Zr- and Hf-doped β-B polycrystalline samples were prepared at the General Electric Research and Development Center by vacuum hot pressing a mixture of powdered β-B (grain size 1–2 μm) and ZrB_2 or HfB_2 (grain size ~ 3 μm) in a BN-lined graphite die at 1900 °C and 6000 psi (400 atm) for 30 min. Subsequently, they were annealed for 3 days under argon at 1800 °C. At the concentrations used (2 at. %), the Zr and Hf ions occupy interstitial sites in the β-B lattice.

The single crystal of YB_{66} used in our thermal-conductivity and specific-heat measurements was also prepared at GE (Ref. 4) and is believed to be slightly nonstoichiometric, the theoretical composition being YB_{68}.[5] Here and in the following we will use the subscript to indicate the starting composition in the crystal-growing process. The thermal conductivity of this sample had been measured previously at Cornell University below 5 K.[6]

The other, also slightly nonstoichiometric $YB_{68-\delta}$ crystals reviewed here, had also been prepared at GE, from the compositions indicated. The YB_{66} and $YB_{61.7}$ samples studied by Bilir,[7] were different from the samples measured at GE (YB_{66} No. R187 and R202, Ref. 8), and also from those measured at Cornell University (YB_{66}, mentioned in the previous paragraph, and $YB_{61.7}$, Refs. 9 and 6).

The thermal conductivity of the Zr- and Hf-doped boron below 100 K was measured with the steady-state temperature-gradient method in a ^{4}He cryostat. Thermal conductivity above 300 K was measured at GE with a commercial apparatus (Dynatech, Cambridge, MA) employing a comparative method.[10] It used stacked short cylinders and a steady guarded heat flow. The thermocouples were embedded at the interfaces. The thermal conductivity of the YB_{66} single crystal was measured at Cornell University between 30 and 300 K with the 3ω method,[11] which is inherently much less susceptible to radiative heat losses than the gradient method near and above room temperature. We refer to Ref. 11 for details.

The specific heat of the YB_{66} sample was measured with the transient heat-pulse method as described by Swartz,[12] using a ^{4}He cryostat which can be inserted into a ^{4}He storage dewar, also described in Ref. 12. The sample (mass 0.661 g) was attached with a polished face to the calorimeter, a sapphire plate sample holder, using a small amount (<2 mg) of N-grease as glue. The heater was a metal film evaporated onto a small sapphire disk which was glued with Elmer's cyanoacrylate adhesive ("Wonder Bond") to the sapphire plate. The plate was suspended with 0.05-mm-diameter Pt:W wires as described previously.[12] The two heater leads, which also served as heat links to the bath, were each made of 2.54-cm-long, 0.127-mm-diameter brass wire soldered to 1-cm-long, 0.127-mm-diameter constantan wire. These lengths of wire gave a sample-to-bath thermal time constant on the order of 10 s at 1.5 K, increasing to roughly 7 min at 40 K, long enough to ensure complete internal equilibration of the sample. The thermometer consisted of a ground-down slice (~ 1 mg) of an Allen-Bradley resistor ($R = 100\ \Omega$ at 300 K), which had been epoxied (Stycast 2850) to a sliver of sapphire. Leads (0.05-mm-diameter Pt:W wire, 2 cm long) were soldered to the remnants of the copper pigtails left in the ground-down resistor, and protected with silver paint. The entire thermometer was covered with epoxy (Stycast 1266) and the sapphire sliver was also attached to the calorimeter plate with Wonder Bond. Total mass of the thermometer (excluding the sapphire) is 10 mg, 6 times larger than that used by Swartz;[12] its advantage is greater resilience to handling and thermal cycling.

The specific heat was measured as follows. After a short heat pulse has been applied to the heater, the exponential decay of the resulting temperature increase $\Delta T(t)$ of the calorimeter is recorded, and the calorimeter-to-cryostat thermal time constant τ is determined. [ΔT is always small ($\sim 2\%$) relative to the cryostat temperature T.] The temperature increase $\Delta T(t)$ is extrapolated to the time the heat pulse was applied, and used to determine the heat capacity (units: erg/K). The heat capacity, divided by the third power of the cryostat temperature T, is shown in Fig. 1. The heat capacity of the empty calorimeter (open circles) is determined largely by the thermometer below 10 K. The heat capacity of the YB_{66} sample (solid triangles), obtained by subtracting the heat capacity of the empty calorimeter (plus N-grease) from that measured with the sample attached, in this case happens to be smaller than that of the empty calorimeter between 5 and 20 K, see Fig. 1. The specific heat of the sample is then obtained by dividing the heat capacity by the mass of the sample.

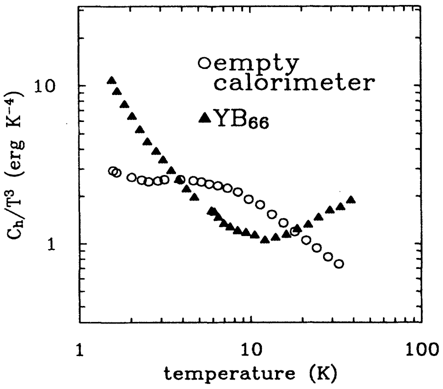

FIG. 1. Heat capacity C_h (units: erg/K) of the empty calorimeter and of the sample, both divided by the cube of the temperature. The sample is a YB_{66} crystal; its specific heat (units: erg $g^{-1}\,K^{-1}$) divided by T^3 is shown in Fig. 7.

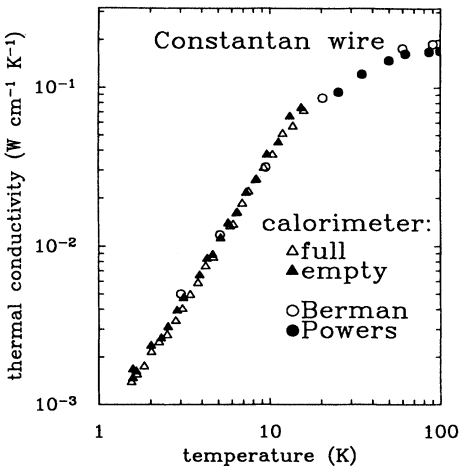

FIG. 2. Thermal conductivity of the constantan wire portion of the heater leads used as heat links between sample holder and cryostat (wire purchased from Driver-Harris and Co., 45 wt. % Ni, 55 wt. % Cu, trace amounts of Fe,Mn,Si); it was determined from calorimeter-to-bath thermal time constants, and the heat capacities from this study (solid circles, full calorimeter; open circles, empty calorimeter), and also from a separate study of $KBr_{0.59}KCN_{0.41}$ (Ref. 13). Thermal conductivity of cupronickel of similar composition from the literature after Ref. 14.

As a test for accuracy of our measurements, we determined the thermal conductivity of the constantan portion of the heater leads which act as a thermal link between sample and bath. This was determined from the measured sample-to-bath time constant, $\tau = R_h C_h$, where R_h is the thermal resistance of the leads and C_h the heat capacity of the sample and/or stage. We used heat-capacity data from the YB_{66} experiment (with heater leads made of constantan wire soldered to brass wire), the empty calorimeter (same leads) and our heat-capacity data from a separate study on $(KBr)_{0.59}(KCN)_{0.41}$ (with heater leads made of brass wire; no constantan, see Ref. 13). The excellent reproducibility of the results demonstrated in Fig. 2 is taken as evidence of the reliability of our method. The data also agree quite well with published data by Berman and by Powers *et al.*[14] shown in Fig. 2. It must be kept in mind, however, that the thermal conductivity of constantan (a cupronickel alloy) depends not only on its composition, but also on its history of prior treatment such as cold-working. Thus, a quantitative comparison with these data should be made with caution.

THERMAL CONDUCTIVITY

The thermal conductivity of pure β-rhombohedral boron above 100 K (Ref. 15) is shown in Fig. 3. It is lower than expected in the temperature range shown by almost a factor of 5. It is, nonetheless, believed to be intrinsic, because of its reproducibility,[8,15] as discussed in Ref. 1. Addition of 2 at. % of Hf or Zr lowers the conductivity above 500 K close to that of amorphous boron reported by Golikova and Tadzhiev,[16] see Fig. 3. As has been suggested by Slack,[3] the thermal conductivity of a given sub-

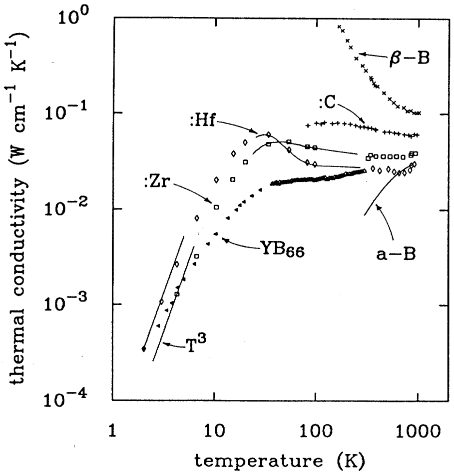

FIG. 3. Thermal conductivity of pure single crystal β-B and of carbon contaminated polycrystalline boron (2.87%), Ref. 15; of polycrystalline boron doped with 2 at. % Hf and Zr, this investigation; of *a*-B (Ref. 16); and of single crystal YB_{66} (Ref. 8; sample *R* 187) from 2 to 200 K, and (different sample) from 30 to 300 K, this investigation. In the temperature range of overlap, the conductivities agree perfectly (another sample measured in Ref. 8, sample *R* 202, however, had a slightly different conductivity, as shown in Fig. 5). At the lowest temperatures, the thermal conductivities of the Zr- and Hf-doped polycrystals approach a T^3 temperature dependence. The solid lines were calculated using a phonon wavelength-independent mean free path of 12 and 4 μm, respectively. A dip can be recognized in the Hf-doped sample near 100 K.

stance in its amorphous phase represents a lower limit, at least above a certain threshold temperature T_{th}. Below T_{th} the thermal conductivity of the glass decreases much less rapidly with decreasing temperature, than does the theoretical lower limit. It has been suggested by Slack that this lower limit, which he called the minimum thermal conductivity, is characterized by a mean free path between collisions of the Debye-like collective excitations which is of the same order as the dimensions of the excitations themselves. This short mean free path leads to a heat transport through a random walk, rather than through traveling waves. Near the softening point of amorphous solids, the vibrating entities are individual atoms, and their sizes increase with decreasing temperatures. This picture has recently been verified for a number of amorphous solids.[11]

Below the threshold temperature T_{th}, the excitations in amorphous solids become more and more wavelike, and their mean free paths approach hundreds of wavelengths at the lowest temperature.[17] We will say more about this threshold below. At this point, we only note that the thermal conductivities of the two doped β-B samples appear to approach the minimum thermal conductivity for boron above 500 K. This indicates very strong phonon scattering.

Below 500 K the conductivity of these doped samples deviates strongly from that of *a*-B; it increases with decreasing temperature, and goes through a maximum near 30 K and 60 K for the Hf- and the Zr-doped boron, respectively. Such a temperature dependence is characteristic for transport by elastic waves. At the lowest temperatures, the conductivities vary approximately as T^3. From the standard expression for the thermal conductivity Λ,

$$\Lambda = \tfrac{1}{3} C \rho v \bar{l} \ , \tag{1}$$

where C is the specific heat (per mass), ρ the mass density, and v the average sound velocity, we can determine the average mean free path $\bar{l}$. At the lowest temperatures, C varies as T^3, and the effect of the doping on the elastic constants should be small. Thus, we use $C\rho = 2.19\times10^{-8}T^3$ J cm^{-3} K^{-4}, and $v = 1.0\times10^6$ cm s^{-1} (the Debye specific heat and velocity of pure β-B) as approximate values for the doped crystals. In the limit of low temperatures, where the thermal conductivity varies as T^3, $\bar{l}$ is thus determined to be ~ 12 and ~ 4 μm for the Hf- and the Zr-doped samples, respectively. These lengths are somewhat larger than the grain sizes of the starting material. However, some grain growth during sample preparation is to be expected.

Above the maximum, the conductivities of the doped samples decrease with increasing temperatures, and in the Hf-doped sample, a sudden change in the slope is suggested at ~ 80 K. Such changes in slope, called "dips," have also been observed previously, e.g., in mixed alkali halide crystals,[18,19] and have been interpreted as resonant scattering by impurity modes. Empirically, the relation between the temperature T_0 of the dip and the resonant angular frequency ω_0 was found to be

$$\hbar\omega_0 = 3.4 k_B T_0 \ , \tag{2}$$

where $\hbar = h/2\pi$ and k_B are Planck's and Boltzmann's constants, respectively. Using the same relation for B:Hf, with $T_0 = 80$ K, we compute $\omega_0 = 3.6\times10^{13}$ rad s^{-1}, or 190 cm^{-1} in the wave-number measure. The theoretical resonance frequency $\omega_{0,\text{theor}}$ can be computed by assuming for simplicity that the resonance is caused by the mass mismatch between a *substitutional* Hf atom (atomic weight $M' = 178$) and the B atom (atomic weight $M = 10.8$). According to Ref. 18 [Eq. (7)], we have

$$\omega_{0,\text{theor}}^2 = \tfrac{1}{3}\omega_D^2 \frac{M}{M'} \ , \tag{3}$$

where ω_D is the Debye frequency which we approximate with that of β-B. From the Debye temperature $\Theta_D = 1540$ K, we determine $\omega_D = 2.02\times10^{14}$ rad s^{-1} (1070 cm^{-1}), and with it from Eq. (3) $\omega_{0,\text{theor}} = 2.9\times10^{13}$ rad s^{-1} (150 cm^{-1}). Considering the crudeness of the model, and also the uncertainty of the experimental data, we would not expect a better agreement. For the lighter Zr atom ($M' = 91$) we would expect the dip to occur at a higher temperature, in qualitative agreement with the experimental findings [we calculate $\omega_{0,\text{theor}} = 4\times10^{13}$ rad s^{-1} (213 cm^{-1}), roughly a 40% increase].

We conclude that in these doped boron crystals the phonons are scattered by grain boundaries at low temperatures, and through resonant scattering by impurity modes at high temperatures. The fact that the thermal conductivity of these crystals approaches that of a-B at high temperatures, indicative of a phonon mean free path of the order of the interatomic spacing, indicates extremely strong scattering. We are unaware of similar scattering resulting from such a small impurity concentration in other host lattices. Part of its cause, undoubtedly, is the large mass mismatch between host and impurity. It is, however, not the only cause. This is demonstrated through the large effect of carbon doping,[15] ($M'=12$), also shown in Fig. 3. At concentrations up to 2 at. %, and possibly even 4 at. %, carbon appears to enter the β-B lattice substitutionally, based on work done at the GE Laboratories. The substitutional carbon leads to free electrons, which may be the cause of the phonon scattering in this case. Note, however, also the very low thermal conductivity in boron carbide,[1] which is not the result of free electrons. These observations demonstrate the high sensitivity of the thermal conductivity of boron or boron-rich borides to their chemical composition.

From a practical point of view, e.g., reducing the parasitic heat flow in thermoelectric applications, it would be important to know by how much the thermal conductivity in doped boron can be decreased (at least in principle) below that observed in the B:2 at. % Hf sample. The obvious approach to answering this question would be to study even higher Hf concentrations, preferably in single crystals. Presumably, the lower limit would be reached with the addition of a few more percent of Hf. Unfortunately, the solubility limit for Zr and Hf lies around 2%, which precludes this approach. As stated above, the thermal conductivity of a-B, at least above the threshold temperature, should be this lower limit. However, there is reason to question the thermal conductivity of a-B shown in Fig. 3: we show the same data in Fig. 4, as the heavy solid line, together with earlier results published by Golikova *et al.*[15] The one point measured near 300 K by Talley *et al.*[20] on a 1.86-mm-diameter a-B deposited on a 25 μm tungsten core lies considerably above the entire range observed by Golikova *et al.*[15,16] There are several possible reasons for this spread in the data. First, it is not clear under what conditions boron is fully amorphous on the atomic scale. It may, for example, also be amorphous only on the scale of the boron icosahedra. Secondly, the microstructure, like cracks or voids, which are frequent in thin layers, may influence the thermal conductivity. All samples measured by Golikova *et al.*[15] were such layers, and some of them showed microcracks and porosity. Finally, thermal conductivity measurements are extremely difficult to perform accurately in this high-temperature range, because of radiative heat losses, in particular on thin layers (nothing is known about the structure or shape of the sample measured in Ref. 16). For a recent critical review of thermal conductivity of thin films, see Cahill *et al.* (Ref. 21). At this point, it thus seems hopeless to decide which of the data in Fig. 4 belong to bulk a-B or, for that matter, how close the doped boron samples come to the theoretical minimum thermal conductivity.

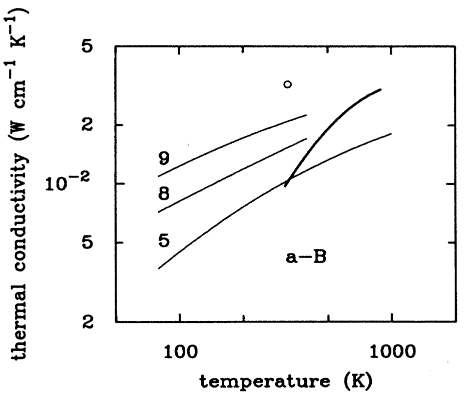

FIG. 4. Thermal conductivities of amorphous boron. Curves labeled 5,8,9 are films, after Golikova *et al.*, Ref. 15; the heavy unlabeled curve after Golikova and Tadzhiev, Ref. 16, unspecified sample geometry. Open circle (335 K, $=3.2\Lambda\times10^{-2}$ W cm^{-1}K^{-1}), after Talley *et al.* (Ref. 20) on a thick cylindrical sample, with radial heat flow.

In light of this uncertainty, it was fortunate that *crystalline* YB_{66}, a nearly stoichiometric substance with the relatively simple crystal structure of YB_{68} (described in Ref. 1), displayed a low-temperature ($0.1<T<300$ K) thermal conductivity which is characteristic for amorphous solids. This phenomenon is also known for several other disordered crystals.[1] This observation led us earlier[1] to suggest that the thermal conductivity of this crystalline substance, which also happens to be available in bulk form, might represent the true conductivity of bulk a-B. In this case, the conductivities observed for a-B, which were lower than those observed for YB_{66}, would have to be caused by microscopic flaws in the a-B. We refer to the discussion in Ref. 1, in particular with regards to a possible structural cause for the glasslike behavior in the YB_{66} crystals, and reproduce in Fig. 3 the earlier results of Slack *et al.* on a sample of YB_{66} (Ref. 8) above 2 K, together with our own data obtained on a different sample between 30 and 300 K, using the 3ω method. The data for the two samples agree perfectly in the temperature region of overlap (30–200 K), thus confirming the earlier measurements. In the following, we will add new data and expand the discussion.

The thermal conductivities above 10 K of three samples of YB_{66}, and of a-B (the same as those shown in Fig. 3) are shown in Fig. 5, together with data for a-SiO_2.[1] Also shown are the theoretical minimum thermal conductivities for YB_{66} and for a-SiO_2, calculated as described in Ref. 11, using the sound velocities of YB_{66} as obtained from Ref. 5 (the theoretical minimum thermal conductivity for B is calculated to be almost identical to that of YB_{66}). The minimum thermal conductivity for SiO_2 agrees well with the experimental data above ~50 K, the so-called threshold temperature for this solid.

For YB_{66}, the data do not extend to sufficiently high temperatures to permit a valid comparison with the model; however, data for GdB_{66} (Ref. 16) appear to join on smoothly to the data for YB_{66}, and agree well with the calculated minimum thermal conductivity. This agreement supports our earlier suggestion that the thermal conductivity of YB_{66} (with GdB_{66} added at this time) is

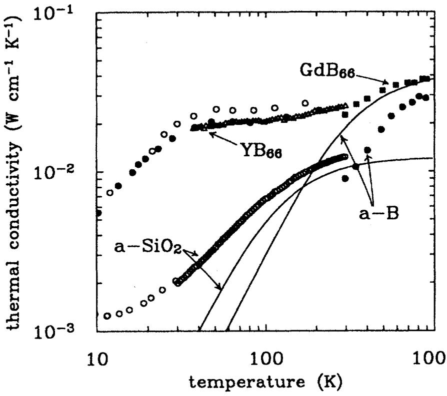

FIG. 5. Thermal conductivity of a-SiO$_2$ (Ref. 11, open circles), a-B (Ref. 16, solid circles, heavy curve in Fig. 4), crystalline YB$_{66}$ [Ref. 8, samples R-187 (solid circles) and R-202 (open circles), and this investigation (open triangles)], and crystalline GdB$_{66}$ (squares) (Ref. 16). The solid curves are minimum thermal conductivities (Refs. 3 and 11) calculated for YB$_{66}$ (very similar to that for a-B), and for a-SiO$_2$.

indeed glasslike.

The deviation of the experimental thermal conductivity from the theoretical minimum conductivity occurs around $T_{\text{th}} = 200$ K. It remains to be understood why T_{th} in these solids occurs at such a high temperature (compared to 50 K for a-SiO$_2$), and why the thermal conductivity in the temperature region of the plateau is so much larger than in all known structural glasses. We suggest that the reason is, quite simply, that the YB$_{66}$ is a much harder substance with a much higher Debye temperature. This leads to a larger minimum thermal conductivity in the limit of high temperatures, as shown in Fig. 5. It also seems plausible that the transition from the random walk to the phonon picture will scale with the Debye temperature, i.e., that the threshold occurs when the Debye-like collective excitations reach approximately the same length in all cases. In YB$_{66}$, T_{th} occurs at $\sim 15\%$ of Θ_D ($=1340$ K), and in a-SiO$_2$ it occurs at 10% of Θ_D ($=500$ K); this is a reasonably close agreement, considering the crudeness of the comparison. The combination of a higher limiting thermal conductivity and a higher transition temperature leads automatically to a higher conductivity in the plateau.

In addition to their characteristic thermal conductivity, all amorphous solids also show an equally characteristic low-temperature specific heat which deviates significantly from the Debye prediction. Earlier measurements by Bilir[7] had explored the question of whether YB$_{66}$ also has such a glasslike specific heat. In the next section, we will report our own measurement, which confirms Bilir's conclusion.

SPECIFIC HEAT OF YB$_{66}$

We have measured the specific heat of the YB$_{66}$ sample between 1.5 and 35 K. Over the entire temperature range a T^3 temperature dependence (as known for Debye solids, and as usually observed in perfect crystals) cannot be discerned, see Fig. 6. The contrast to pure β-B (Refs. 12, 1, and 2) is striking. The dashed line represents the Debye low-temperature prediction for β-B, based on ultrasonic measurements.[22] The contrast is shown even more clearly in Fig. 7, in which the specific heat divided by T^3, is plotted versus T, also on logarithmic scales. The two dashed lines are the Debye predictions for the two solids. They are $C = 5.1\times10^{-8}T^3$ J g^{-1} K^{-4} for β-B ($\Theta_B = 1540$ K, $v_D = 1.01\times10^6$ cm s^{-1}, Ref. 22, and mass density $\rho = 2.329$ g cm^{-3}), and $C = 6.71\times10^{-8}T^3$ J g^{-1} K^{-4} for YB$_{66}$ ($\Theta_{\text{YB}_{66}} = 1340\pm50$ K, calculated from the elastic constants given in Ref. 5, from which $v_D = 9.0\times10^5$ cm s^{-1}; $\rho = 2.568$ g cm^{-3}). The almost perfect agreement with the Debye prediction for β-B below 20 K (0.013 Θ_D) is contrasted by a rapid rise noticed for YB$_{66}$ below 10 K, and by the fact that the YB$_{66}$ specific heat exceeds the Debye low-temperature limiting value over the entire temperature range. This behavior is very similar to that observed in amorphous solids.[23] Furthermore, the fact that the rapid rise of C/T^3 above 10 K sets in at a lower temperature than in the β-B, is additional evidence for glassy behavior. It is frequently observed that the hump in C/T^3, which in crystalline solids indicates a higher phonon density of states of the lowest acoustic modes at the Brillouin-zone boundary, is shifted to lower temperatures in the amorphous phase.[24,25] We interpret the rise observed in YB$_{66}$ as the beginning of this hump.

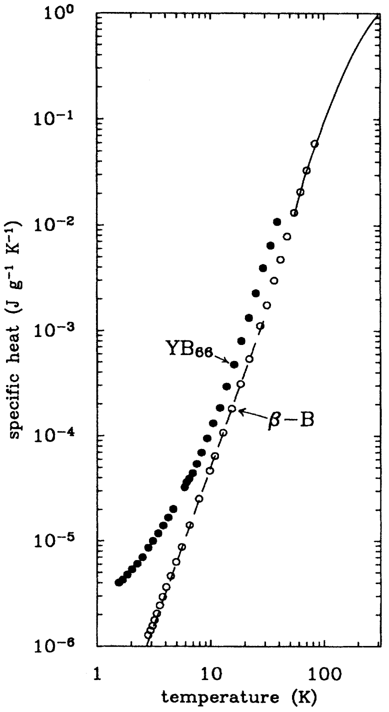

FIG. 6. Specific heat of β-B (below 100 K, Ref. 12, solid line above 50 K, after Johnston, reviewed in Refs. 1 and 2) and of YB$_{66}$ (this investigation).

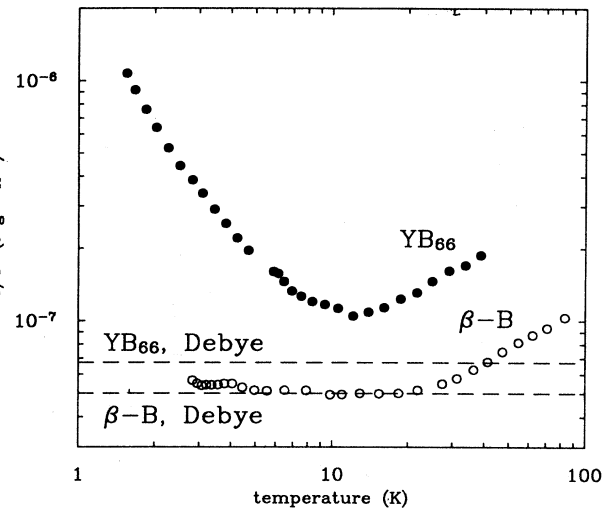

FIG. 7. Specific heat of crystalline YB_{66} and β-B, divided by T^3, compared to the Debye predictions (dashed lines, using $\Theta_B=1540$ K, and $\Theta_{YB_{66}}=1340$ K). The rise above 20 K in β-B is believed to be the beginning of a hump peaking at around 100 K, see Ref. 2.

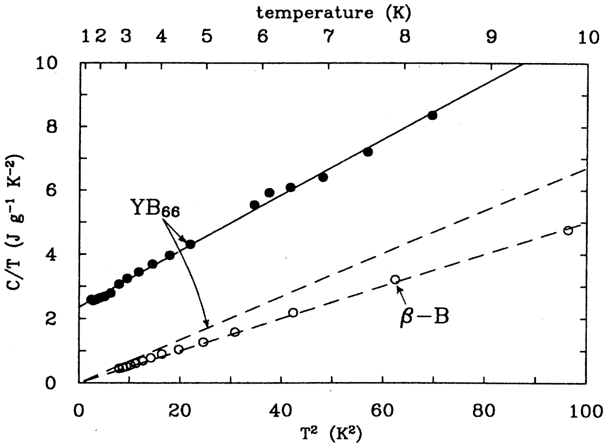

FIG. 8. Specific heat C divided by T plotted vs T^2 on linear scales, to test Eq. (4). Dashed lines: Debye predictions. The data points for YB_{66} yield $c_1=23$ erg g^{-1} K^{-2} and $c_3+c_D=0.89$ erg g^{-1} K^{-4}.

In amorphous solids, the specific heat has been found empirically to be described at low temperatures (i.e., below the minimum of the C/T^3 versus T plot) by a polynomial of the form

$$C=c_1T+(c_3+c_D)T^3 \ . \tag{4}$$

If C/T is plotted versus T^2 on linear scales, a temperature dependence of the form of Eq. (4) is given by a straight line; its slope is (c_3+c_D), its intercept with the vertical axis (at $T=0$) is c_1. In Fig. 8, we plot the specific heats of β-B and of YB_{66} in this form below $T=10$ K, which is the temperature of the minimum of the C/T^3 plot for YB_{66}, Fig. 7. The dashed lines are the Debye predictions for the two crystals. For β-B, the intercept is zero, and the slope agrees with c_D. This behavior is typical for a Debye solid. For YB_{66}, the data also fit a straight line, which, however, does not go through the origin. Thus, the specific heat is of the form of Eq. (4). From the intercept, we determine $c_1=23$ erg g^{-1} K^{-4}, and $c_3+c_D=0.89$ erg g^{-1} K$^{-4}=1.33c_D$. The values for c_1 and c_3 lie in the range typical for amorphous solids.[23] Thus, our specific-heat measurements support the earlier conclusion by Bilir *et al.*[7] that the thermal properties of YB_{66} are indeed very similar to those of glasses. For a further discussion of glasslike properties in crystalline solids, and for a possible explanation of their origins, we refer to Ref. 1.

Bilir's data, obtained for different samples (but also prepared at GE) of nominal compositions $YB_{61.7}$ and YB_{66}, and of β-B, are plotted in Fig. 9, together with our own data. The comparison is simultaneously encouraging and disappointing. Below 5 K, the data agree well with our data, and suggest that all samples have a linear specific-heat anomaly with very similar c_1's. Above 5 K, however, Bilir's data deviate abruptly from ours. By the abruptness of this change, and from the fact that it sets in at the same temperature in all three cases, we are tempted to infer experimental troubles in Bilir's setup (for a similar discrepancy, and our attempts to locate its origin, see Ref. 26). However, unless the samples could be exchanged and remeasured, which appears unrealistic at this time, a sample dependent specific heat as another source of the discrepancy cannot be excluded.

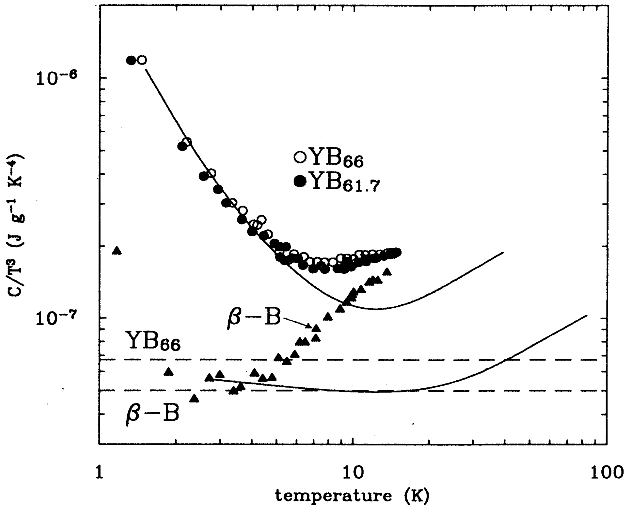

FIG. 9. Comparison of the Cornell University data on YB_{66} and β-B shown in Fig. 7 (solid lines) with data obtained by Bilir *et al.* (Ref. 7). The data agree below ~5 K (the rapid rise of the data of β-B by Bilir below 2 K is believed to be caused by impurities similar to anomalies seen at Cornell, although the anomaly is somewhat larger in the former). The origin of the discrepancy between the Cornell University data and Bilir's data above 5 K is not clear, see text.

CONCLUSIONS

While very strong phonon-resonant scattering has been found in β-B containing modest amounts of impurities, the question of the minimum thermal conductivity of boron-rich solids, and also of the thermal conductivity of amorphous boron, is still unresolved. More evidence has been accumulated for glasslike thermal properties in crystals of YB_{66}, $YB_{61.7}$, and GdB_{66}. It may thus be hoped that the question of the minimum thermal conductivity in boron or in boron-rich borides (like the boron carbides) can be answered by studying borides of the crystal structure of YB_{68}, in addition to studying β-B doped with varying concentrations of heavy atomic impurities, and also bulk a-B if it becomes available.

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