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Thermal properties of a tetrahedrally bonded amorphous solid: $CdGeAs_2$

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We have measured the low-temperature thermal conductivity and specific heat of $CdGeAs_2$ to investigate the influence of coordination number on the thermal properties of amorphous solids. $CdGeAs_2$ is tetrahedrally bonded in the crystalline state and strong evidence exists that this local order is preserved in the amorphous state. The thermal conductivity of the amorphous material was measured from 0.1 to 300 K. It displays the same behavior as all other glasses: a T^2 dependence below 1 K, a wide range of temperature over which the conductivity is approximately temperature independent, and a thermal conductivity at high temperatures that approaches the minimum thermal conductivity as described by Slack. The specific heats of *c*-$CdGeAs_2$ and *a*-$CdGeAs_2$ were measured from 0.1 to 50 K. Below 1 K, the amorphous material shows the excess specific heat that is characteristic of amorphous solids. Above 1 K, the specific heat of the amorphous material, when compared to the Debye model, closely resembles the specific heat of the crystal. We have also measured the thermal conductivity of a sputtered film of *a*-Ge from 30 to 300 K and compare our results to previous measurements of the thermal properties of *a*-Si and *a*-Ge. On the basis of our experimental findings, we conclude that the thermal properties of amorphous solids do not depend on the coordination number.

I. INTRODUCTION

The vibrational properties of amorphous solids differ from those of crystalline solids in many ways; tunneling states dominate the low-temperature thermal properties of amorphous solids, the specific heat is larger than predicted by the Debye model, and the thermal conductivity above 10 K shows that the mean free path of the majority of phonons is very short, on the order of the phonon wavelength.[1] In this paper we discuss the effects of the coordination number of the amorphous solid on these properties, i.e., are these experimental signatures of amorphous materials truly universal, or do we find exceptions in tetrahedrally bonded solids, as *a*-Si and *a*-Ge. The reason we might expect *a*-Si and *a*-Ge to differ from other amorphous solids has often been summarized by a simple statement: If every atom is bonded to four of its neighbors, the lattice should be overconstrained, and thus the atomic motion postulated to explain the tunneling states and other low-temperature properties should be much less likely.[2] Thorpe and his co-workers have recently stressed the importance of coordination number for the vibrational properties of amorphous solids.[3]

To answer these questions, especially with regard to the existence of tunneling states as an intrinsic excitation, the thermal properties of *a*-Si and *a*-Ge below 10 K have been the subject of many investigations. The experimental situation is still not clear. While tunneling states are observed in many experiments, some authors have attributed their existence to the intrinsic properties of the amorphous lattice[4,5] while others have suggested that the tunneling states arise from defects such as the surfaces of voids and dangling bonds.[6,7] These studies of *a*-Si and *a*-Ge have been made difficult by the fact that Si and Ge do not form bulk glasses; thin films of *a*-Si and *a*-Ge are produced by evaporation or sputtering or as hydrogenated material produced by glow discharge. The complex morphology of these films is an active area of research.[8]

In this work we describe measurements of the thermal properties of a tetrahedrally bonded compound $CdGeAs_2$ that forms bulk glass when the liquid is quenched rapidly. In addition to exploring the question of coordination number in amorphous solids, we mention another reason for the study of $CdGeAs_2$. The tetrahedrally bonded amorphous solids have a relatively simple structure. These materials have a large degree of short-range order, each atom is bonded to four of its neighbors in a geometry resembling the crystalline state and are therefore particularly attractive materials for the study of the structure and vibrational properties of amorphous solids. A structural model has emerged, the continuous random network,[9] which leads to good agreement with the measured radial distribution function, and, for *a*-Si and *a*-Ge, with the spectrum of lattice vibrations measured by Raman and FIR studies.[10] With $CdGeAs_2$, the vibrational properties of a tetrahedrally bonded network can be studied in a bulk sample, free from the complicated morphology of thin films.

II. $CdGeAs_2$ STRUCTURE

$CdGeAs_2$ crystallizes in the chalcopyrite structure, the ternary analog of zinc blende. The chalcopyrites have shown promise for application in nonlinear optics and energy conversion; these compounds are the subject of an extensive monograph[11] and bibliography.[12] Vaipolin *et al.* discovered the amorphous phase of $CdGeAs_2$ and suggested on the basis of density measurements that the short-range order of the crystal is preserved in the glass.[13] The density of the glass is 2% larger than the crystal,[14] in contrast to most glasses in which the density is smaller than in the crystalline form. Červinka, Hosemann, and Vogel[14] pointed out that $CdGeAs_2$ is one member of a large family of glass-forming materials based on $CdAs_2$.[15] Of these systems, $CdGe_xAs_2$ forms a glass over the largest range of x: $0.02 < x < 1.3$. Risbud studied the microstructure of a-$CdGeAs_2$ and observed glass-in-glass phase separation on a scale of 40 nm.[16]

How confident can we be that a-$CdGeAs_2$ is tetrahedrally coordinated? In general, the short-range order of an amorphous solid is difficult to determine. We know of three studies that have addressed this problem for $CdGeAs_2$. Popescu, Mănăilă, and Grigorovici[17] found good agreement between a continuous-random-network model of tetrahedrally coordinated atoms and the measured radial distribution function.[17] Mössbauer studies of ^{57}Fe-doped $CdGeAs_2$ were interpreted as evidence that at least for the Cd site, the short-range order is the same in the crystal and the glass.[18] EXAFS studies of the As atoms give strong evidence that this is true for As as well.[19]

III. EXPERIMENTAL MATTERS

We prepared our $CdGeAs_2$ samples from 99.9999%-pure Cd and As and 99.9995%-pure Ge purchased from Alpha Chemicals; we followed the procedure outlined by Di Salvo *et al.*[20] Crystalline samples were produced by reacting the elements in an evacuated silica tube which was sealed in a second silica tube. The crystalline samples were checked by x-ray powder diffraction. We found only the diffraction pattern characteristic of the chalcopyrite structure.[21] A few grams of the crystalline material were placed in 3-mm-inner-diameter, 4-mm-outer-diameter silica tubes for preparing the glass samples. The tubes were heated to 1100 K and then rapidly quenched into a water bath. To help prevent the a-$CdGeAs_2$ from sticking, the tubes were first coated with a carbon film produced by thermal decomposition of acetone vapors. The samples were checked by x-ray powder diffraction to insure that they were fully amorphous.

Thermal conductivity of a-$CdGeAs_2$ below 30 K was measured with the steady-state temperature-gradient method using one heater and two thermometers. Above 1.5 K, we used 160-Ω Allan-Bradley carbon resistors as thermometers, below 1.5 K we chose 200-Ω Matsushita carbon resistors.[22] Samples were 3 mm in diameter and approximately 2 cm long. As an added precaution the surface of the sample used below 1.5 K was sandblasted to ensure diffuse phonon scattering.

Specific-heat measurements below 1 K were performed with the transient-heat-pulse technique also used previously at Cornell.[23] Thermal sample-to-bath time constants were typically a few seconds. The polycrystalline $CdGeAs_2$ sample had a mass of 6 g. Four pieces of a-$CdGeAs_2$, 3 mm in diameter and 1.5 cm long, were glued together using GE 7031 varnish to produce a sample of 2 g. We prepared a small-heat-capacity thermometer by grinding down a 100-Ω Matsushita carbon resistor. The thermometer was first flattened on one side and then glued to a sapphire wafer, mass ~40 mg, with Stycast 2850 epoxy. The thermometer was then polished to a thickness of 0.2 mm to improve its equilibration time at low temperatures. We soldered leads to the exposed copper stubs and, as added precaution against changing electrical contact, we coated the ends of the thermometer with silver paint and covered the top of the entire assembly with Stycast 1266 epoxy. Total mass of the thermometers was ~10 mg, excepting the sapphire wafer. The thermometers were attached to the sample with GE 7031 varnish. A thin film of Constantan evaporated onto another sapphire wafer served as the sample heater. Leads to the heater and thermometer were made from Cu-clad Nb:Ti wire of 2-mil diameter. The Cu cladding was removed except for a 5-mm length at each end to allow soldered electrical connections.

To test our technique for the measurement of specific heat below 1 K and to determine the heat capacity of the addenda (the thermometer, heater, and adhesives used to attach them) we measured the heat capacity of a 1.03-g sample of single-crystal NaCl and a 2.31-g sample of single-crystal KBr. The KBr sample was taken from the same piece that was shown by Knaak and Meissner[24] to have a specific heat that followed the Debye prediction to 0.1 K. (The crystal is from Cornell boule no. 224.) Our results are shown in Fig. 1. The solid line marked "addenda" is the difference between the measured heat capa-

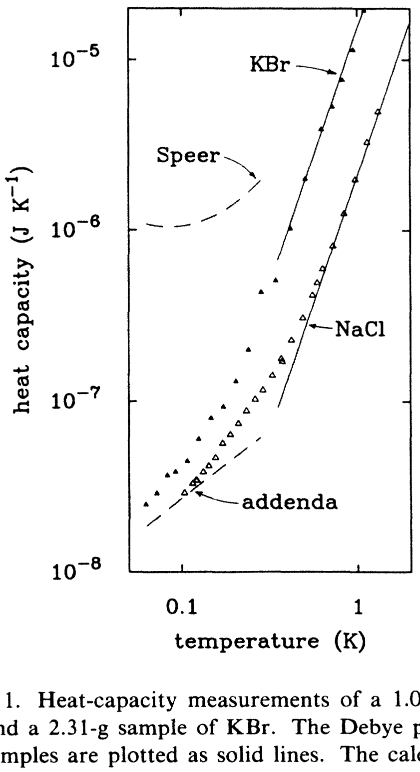

FIG. 1. Heat-capacity measurements of a 1.03-g sample of NaCl and a 2.31-g sample of KBr. The Debye predictions for these samples are plotted as solid lines. The calculated Debye heat capacities are extrapolated from measurements at higher temperatures: for NaCl, see Ref. 25, $\Theta_D = 321$ K, $C_D = 2.01T^3$ $\mu J\,g^{-1}\,K^{-1}$. For KBr see Ref. 26, $\Theta_D = 172$ K, $C_D = 6.41T^3$ $\mu J\,g^{-1}\,K^{-1}$. The dashed line marked "addenda" is the heat capacity of our sample addenda determined from the deviation of the measured data from the Debye prediction. The curve marked "Speer" is the heat capacity of a 30-mg carbon chip cut from a Speer 220 Ω resistor from Ref. 29.

city and the Debye specific heat for both crystals. This addenda contribution is consistent with both measurements and is comparable to the heat capacity measured by Steinback, Anthony, and Anderson[22] for a Matsushita resistor ground down to a mass of 11 mg. Speer resistors were used for previous low-temperature specific-heat work at Cornell[23,27,28]; the heat capacity of a ~30-mg chip cut from a Speer 220-Ω resistor is shown as a dashed line.[29] The small-heat capacity of the Matsushita resistor clearly facilitates the measurement of small-heat capacities at low temperatures.

The technique and equipment used for the specific-heat measurements above 2 K have been described in detail by Swartz.[30] Our samples had a mass of a few tenths of a gram. The heat capacity of the platform was subtracted from the measured heat capacities. The heat capacity of the addenda was less than 10% of the measured-heat capacity.

For the thermal-conductivity measurements above 30 K, we used a new ac technique that we call the 3ω method. This technique has been described in detail elsewhere.[31] The a-CdGeAs$_2$ sample was a 0.3×1.5-cm^2 cylinder that was flattened on one side to accommodate the narrow, evaporated silver line that serves as the heater and thermometer in this measurement. The line was 8 mm long and approximately 0.1 mm wide and was produced by evaporation through a mask. The a-Ge sample was a 50-μm-thick film produced by sputtering onto a glass substrate. By using a 5-μm-wide silver line as the heater and thermometer, and by using sufficiently high frequencies so that the thermal wave is completely contained within the 50-μm film, the thermal conductivity of the a-Ge film can be measured free from any contribution from the substrate. The 5-μm-wide line was produced by photolithography.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The thermal conductivity of a-CdGeAs$_2$ is plotted in Fig. 2 with data for a-As$_2$S$_3$ and a-SiO$_2$ for comparison.[28,31–34] As is observed in all other glasses, the data below 1 K show a T^2 temperature dependence, evidence for resonant scattering of phonons by tunneling states.[37] The magnitude of the T^2 conductivity falls within the surprisingly small range of observed thermal conductivities of amorphous solids at low temperatures; a-SiO$_2$ and a-As$_2$S$_3$ almost span the range of observed conductivities below 1 K. [CaK(NO$_3$)$_3$ glass has a thermal conductivity 30% lower than a-SiO$_2$ below 1 K.] Thus the tetrahedrally bonded a-CdGeAs$_2$ is a typical glass as far as the thermal conductivity below 1 K is concerned.

In the temperature interval 5–20 K, the thermal conductivity of amorphous solids is nearly temperature independent. This characteristic feature is often referred to as the plateau. The thermal conductivity of most amorphous solids increases again above 20 K, as demonstrated by the data for a-SiO$_2$. We do not observe this increase in a-CdGeAs$_2$. The tetrahedral coordination in a-CdGeAs$_2$ is a tempting explanation for this result but a comparison to a-As$_2$S$_3$, where the average coordination is 2.4, makes a dependence on the coordination number unlikely. The data for a-As$_2$S$_3$ also show only a very slight increase above 20 K.

The absence of an increase of the thermal conductivity above 20 K for a-CdGeAs$_2$ and a-As$_2$S$_3$ can be understood by viewing the plateau as a transition between the low-temperature conductivity dominated by tunneling states to the minimum conductivity[38] at high temperatures. In SiO$_2$, for example, the magnitude of the conductivity at the plateau is a factor of 10 smaller than the value of the minimum conductivity at room temperature. The conductivity must increase past the plateau to reach the minimum conductivity at high temperatures. In a-CdGeAs$_2$ and a-As$_2$S$_3$ the magnitude of the conductivity at the plateau is already comparable to the minimum conductivity at room temperature. Therefore, no increase in the conductivity with increasing temperature is required.

Since the atomic masses of the constituents and the short-range order in a-CdGeAs$_2$ are similar to a-Ge, we can expect that the thermal conductivities will be similar as well. Figure 3 shows that this is indeed the case. The thermal conductivity of a-CdGeAs$_2$ is plotted with our high-temperature measurements of a sputtered film of a-Ge and with low-temperature measurements taken from the literature.[5,6] Above 30 K, the thermal conductivities of a-Ge and a-CdGeAs$_2$ have a very similar magnitude and temperature dependence. In this high-temperature

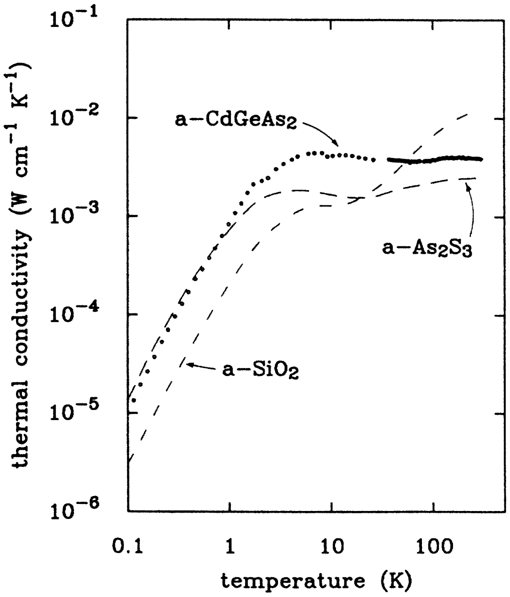

FIG. 2. Thermal conductivity of amorphous CdGeAs$_2$ with a-SiO$_2$ and a-As$_2$S$_3$ for comparison. Data for a-SiO$_2$, below 1 K, Ref. 32; 1–30 K, Ref. 33; 30–300 K, Ref. 31. Data for a-As$_2$S$_3$, below 1 K, Ref. 28; 1–30 K, Ref. 34; 30–300 K, Ref. 31. Above 200 K, our data for a-CdGeAs$_2$ agree with Osmanov *et al.*, Ref. 35, but are a factor of three smaller than data from Ref. 36. A fit to the data between 0.1 and 0.3 K gives $\Lambda=1.25T^{2.08}$ mW cm^{-1} K^{-1}. The kink in the data for a-CeGeAs$_2$ around 1.5 K results from geometry error for the sample used below 1.5 K and the sample used above 1.5 K. The kink in the data around 10 K is within the errors of the measurement.

regime, where the phonon mean free path is a few atomic spacings, we expect the data to be insensitive to the morphology of the Ge film. Below 10 K, however, the thermal conductivity can be strongly affected by the structure of the films as can be seen by examining Fig. 3. The lower curve for *a*-Ge, marked LS, is the data for the lowest thermal-conductivity measured by Löhneysen and Steglich on a series of evaporated *a*-Ge films.[5] The other curve for *a*-Ge, marked GA, is for the highest-density film measured by Graebner and Allen.[6] We agree with the interpretation of Graebner and Allen that the thermal conductivity of *a*-Ge is strongly influenced by the presence of voids and other more complicated structures in the evaporated films. These structures result in the order of magnitude difference in the conductivities of (GA) and (LS). The data for *a*-$CdGeAs_2$ are presumably free from this source of phonon scattering since *a*-$CdGeAs_2$ is produced by melt quenching and therefore avoids the complicated structures associated with evaporated films.

Graebner and Allen observed that the thermal conductivity increased with increasing density of the *a*-Ge films. (We mention that their highest density film, plotted in Fig. 3, contained 3 at. % oxygen. Graebner and Allen did not, however, observe any correlation between oxygen content and the thermal conductivity of their films.) In comparing their data to the thermal conductivity of *a*-$CdGeAs_2$, we infer that for their highest-density films they observed the low-temperature thermal conductivity intrinsic to *a*-Ge; thus we will speculate that fully dense *a*-Ge, if it could ever be prepared as a thin film or in bulk, would also show evidence of strong phonon scattering by tunneling states. We note the almost identical magnitude of the two measured thermal conductivities in spite of the great difference in the methods used to produce the samples: quenching of the melt for *a*-$CdGeAs_2$ and evaporation for *a*-Ge.

The thermal conductivity at high temperatures is shown more clearly in Fig. 4. The existing data for *a*-Ge near room temperature (not shown) show a great deal of scatter. We measure $\Lambda_{a\text{-Ge}} = 5.1$ mW cm^{-1} K^{-1}, results from Ref. 41 give $\Lambda_{a\text{-Ge}} = 26$ mW cm^{-1} K^{-1} and Ref. 42 gives $\Lambda_{a\text{-Ge}} = 120$ mW cm^{-1} K^{-1}. We feel that this scatter emphasizes the difficulty in measuring the thermal conductivity of poorly-conducting materials at elevated temperatures, a difficulty which is even increased for thin films. The 3ω method has been shown to give reliable results in this difficult experimental regime.[31] In Fig. 4 we also plot the calculated minimum thermal conductivity as suggested by Slack.[38] According to this picture, the minimum thermal conductivity is reached when each Debye phonon has a mean free path of one-half of its wavelength. The origin of this strong scattering is not known. The degree of quantitative agreement at room temperature, shown in Fig. 4, is typical.[31] Below 50 K, the model predicts a minimum thermal conductivity that drops rapidly with decreasing temperature. That the measured thermal conductivity falls off much less rapidly indicates that the phonon scattering diminishes, i.e., the mean free path grows. Below a few K, the mean free path of phonons in amorphous solids is of the order of 100 wavelengths.[32]

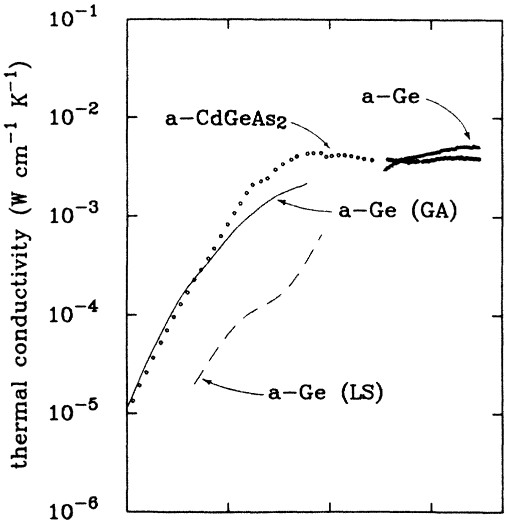

FIG. 3. Thermal conductivity of amorphous $CdGeAs_2$ and *a*-Ge. The data above 30 K for *a*-Ge are for a 50-μm-thick film prepared by sputtering and measured using the 3ω method. Data for *a*-Ge below 10 K were obtained on films prepared by evaporation. Data labeled (GA) are for the most dense film from Ref. 6; data labeled (LS) are for the sample with the lowest thermal conductivity in Ref. 5.

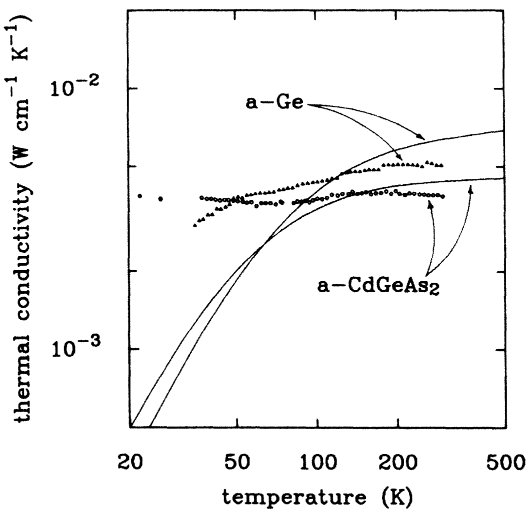

FIG. 4. Thermal conductivity at high temperatures for *a*-$CdGeAs_2$ and *a*-Ge. Solid lines are the calculated minimum thermal conductivity, assuming a mean free path of one-half of a wavelength for all Debye phonons. Details in Ref. 31. Speeds of sound in *a*-$CdGeAs_2$ are from Ref. 39; $v_l = 3.03$ km sec^{-1}, $v_t = 1.86$ km sec^{-1}. The density of *a*-$CdCeAs_2$, $\rho = 5.72$ g cm^{-3}, gives an atomic density of 4.11×10^{22} cm^{-3}. The speeds of sound in *a*-Ge were estimated to be 82% of the crystalline values as described in Ref. 40; $v_l = 4.35$ km sec^{-1}, $v_t = 2.63$ km sec^{-1}. Using the density of crystalline Ge, $\rho = 5.32$ g cm^{-3} gives an atomic density of 4.41×10^{22} cm^{-3}.

The specific heat below 1 K also gives evidence for the existence of the tunneling states characteristic for amorphous solids. The specific heats of the glass and crystal are plotted in Fig. 5 for the full temperature range of our measurements. (Bohmhammel, Deus, and Schneider[43] measured the specific heat of c-CdGeAs$_2$ above 4 K; our results are in good agreement.) The specific heat of a-CdGeAs$_2$ has a contribution, evident below 1 K, with an approximately linear temperature dependence and a magnitude that is comparable to the linear term observed in other amorphous solids. The glass sample also shows a small-specific-heat hump peaking around 0.2 K that we believe to arise from impurities. For comparison, we also plot the low-temperature specific heat[28] of As$_2$S$_3$, a glass whose linear specific heat is typical of amorphous solids. We mention in passing that the specific heat of a-As was originally interpreted as evidence against tunneling states in the threefold coordinated solid since it appeared to show no low-temperature anomaly.[44] More recent measurements at lower temperatures have, however, revealed the excess specific heat.[45]

Below 0.3 K, our sample of crystalline CdGeAs$_2$ also deviates from the T^3 dependence that is expected for insulating crystalline solids. We feel that a likely explanation for this anomaly is the nuclear quadrupole moment of the As atoms as was suggested by Jones, Phillips, and Lasjaunias[45] to explain an anomaly of almost equal magnitude in the specific heat of a-As. The observed specific-heat anomaly in a-As was only a fraction of the calculated nuclear specific heat, presumably due to the very long time, ~2000 sec, required for the nuclei to reach thermal equilibrium. Supporting this interpretation, we observed nonexponential decays of the heat pulses below 0.1 K in c-CdGeAs$_2$, and many hours were required for the sample to reach thermal equilibrium when the sample was cooled quickly from 0.4 to 0.1 K. These effects were not observed during our measurement of amorphous CdGeAs$_2$. The nuclear moments of As in c-CdGeAs$_2$ probably relax fast enough to affect our specific-heat measurements but As in a-CdGeAs$_2$ seems to have a relaxation time that is much longer, long enough to prevent the nuclear specific heat from appearing in our data.

The specific-heat anomaly in glasses is often approximated by the polynomial

$$C_p = c_1 T + (c_D + c_3) T^3 ,$$

where $c_1 T$ and $c_3 T$ are the linear and excess T^3 anomalies, respectively, and $c_D T^3$ is the Debye phonon specific heat based on elastic data. In Fig. 6 we plot the low-temperature specific heat as C_p/T versus T^2; the slope of the straight-line fit gives $c_3 + c_D$ and the intercept gives c_1. The Debye prediction $C_p = c_D T^3$ is plotted as a solid line. To calculate the Debye specific heat of the crystal, we used the Debye temperature determined from the elastic constants $\Theta_{D,\text{cryst}} = 257$ K,[46] and find close agreement with the experimental data (see Figure caption for details). The Debye temperature of the glass, calculated from the measured speeds of sound[39] at room tem-

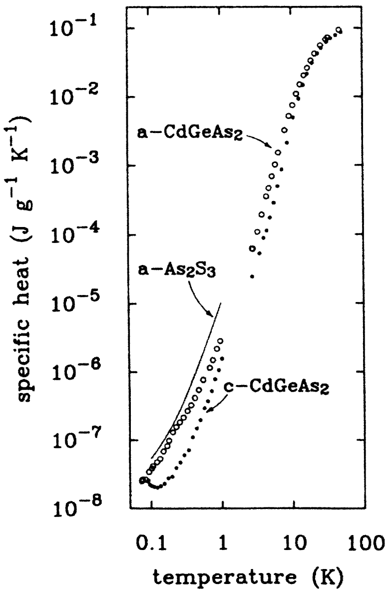

FIG. 5. Specific heat of crystalline and amorphous CdGeAs$_2$. Solid line for As$_2$S$_3$ is for comparison, Ref. 28.

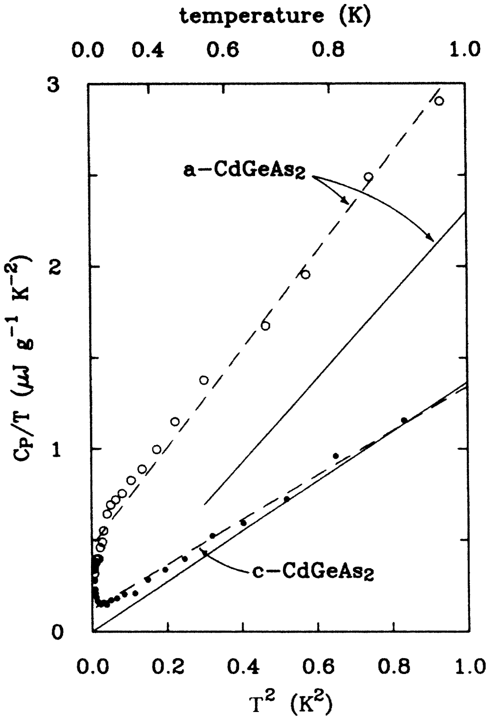

FIG. 6. Specific heat of crystalline and amorphous CdGeAs$_2$ plotted as C_p/T vs T^2 to fit the data to the equation $C_p = c_1 T + (c_D + c_3) T^3$. The solid lines are the Debye predictions using the measured elastic constants. For crystalline CdGeAs$_2$, see Ref. 46; $\Theta_{D,\text{cryst}} = 257$ K, $c_D = 1.37$ μJ g^{-1} K^{-4}. For amorphous CdGeAs$_2$ see Ref. 39; $\Theta_D = 216$ K, $c_D = 2.30$ μJ g^{-1} K^{-4}. Dashed lines are fits restricted to the data between 0.1 and 1 K. The functional form of this fit becomes an increasingly poor approximation to the data below 0.1 K; for c-CdGeAs$_2$, $c_1 = 0.12$ μJ g^{-1} K^{-2}, $(c_D + c_3) = 1.22$ μJ g^{-1} K^{-4}; for a-CdGeAs$_2$, $c_1 = 0.47$ μJ g^{-1} K^{-2}, $(c_D + c_3) = 2.68$ μJ g^{-1} K^{-4}.

perature and extrapolated to 0 K is 216 K. This can be compared to the Debye temperature of 203 K determined by Thompson and Bailey[47] for the closely related nonstoichiometric compound a-$Cd_6Ge_3As_{11}$.[47] (Thompson and Bailey studied this compound instead of a-$CdGeAs_2$ because it can be quenched in much larger samples.)

The data for a-$CdGeAs_2$ deviate from a straight line at the lowest temperatures; the data drop below a straight-line fit for $T<0.2$ K. As has been observed in other glasses, the specific heat below 0.2 K can be interpreted as following a power law $C_p \sim T^n$ with $n>1$. The limited temperature range of our data and the appearance of a small hump in the data just above 0.2 K make the value of n uncertain but a fit to the data between 0.07 and 0.15 K gives $n=1.4$. (For comparison, data for SiO_2 (Ref. 48) give $n=1.2$ and data for B_2O_3 (Ref. 49) give $n=1.45$.) We cannot conclude that the entire excess specific heat of a-$CdGeAs_2$ at low temperatures is intrinsic. The specific heats of a-SiO_2 (Ref. 48) and a-As_2S_3 (Ref. 28) have been shown to depend on purity of the samples. The similarity of the specific heat of a-$CdGeAs_2$ to other glasses, however, allows us to take the approximately linear specific heat observed in a-$CdGeAs_2$ as additional evidence for the tunneling states observed in the thermal-conductivity data.

Figure 7 shows the data above 0.5 K plotted as C_p/C_D versus T/Θ_D to highlight the deviation of the measured specific heat from the Debye prediction. We see that both the crystalline and amorphous specific heat have a peak at $\sim\Theta_D/20$ where the specific heat exceeds the Debye value by a factor of 3. A peak in C_p/C_D in this temperature range for crystalline materials can usually be ascribed to the increased density of states resulting from zone boundary dispersion of the TA phonons. This effect is quite large in Ge and Si due to the flattened dispersion curve for TA phonons in the diamond structure.[50] Presumably, this is also true in the closely related chalcopyrite structure of $CdGeAs_2$. When scaled in the manner used in Fig. 7, the specific heat of the glass appears almost identical to the crystal; the specific heat at $\Theta_D/100$ exceeds the Debye prediction by only $\sim 30\%$ and the magnitude of the T^3 term (c_D+c_3) found from the fit to the data in Fig. 6 exceeds the Debye value by only $\sim 15\%$. We infer from this observation that the vibrational density of states of the glass and crystal are closely related. This similarity of glass and crystal is also observed[40,51] in the specific heat of Si and Ge although a reliable calculation of C_D for a-Si and a-Ge is difficult since the speeds of sound are strongly influenced by the film structure.[52] When compared to the crystalline specific heat, the peak in C_p/T^3 for most glasses is considerably larger and shifted downward in temperature. This feature, which had been thought to be a general property of amorphous solids,[53] is not demonstrated by $CdGeAs_2$. More data on materials that can be prepared both in crystalline and amorphous forms are needed before any conclusions can be made regarding the possible effect of coordination number on the additional excitations observed above 1 K.

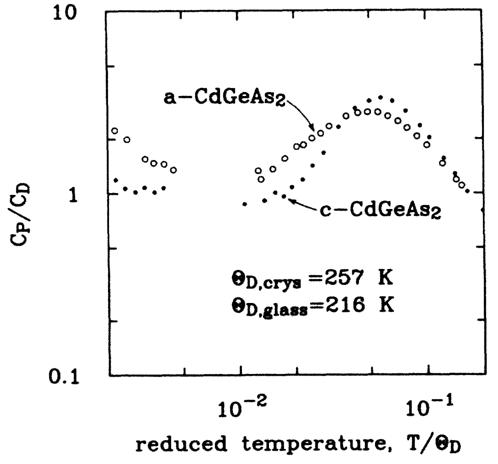

FIG. 7. Specific heat of crystalline and amorphous $CdGeAs_2$ plotted as the deviation from the Debye prediction vs the reduced temperature.

Using the magnitude of the linear specific heat, the Debye temperature of the glass, and the magnitude of the T^2 thermal conductivity, we can estimate the parameters in the tunneling model.[54] We assume the shortest-tunneling-state relaxation time $\tau_{\min}$ to be 10 μsec, which is close to the value calculated for a-SiO_2 at 0.1 K (Ref. 55). $\bar{P}$ depends only logarithmically on the choice of $\tau_{\min}$. We find for a-$CdGeAs_2$ the density of states $\bar{P}=2.0\times10^{20}$ $eV^{-1}cm^{-3}$ and coupling constant $\bar{\gamma}=0.38$ eV. For comparison we calculate in the same way $\bar{P}=1.8\times10^{20}$ $eV^{-1}cm^{-3}$ and $\bar{\gamma}=0.80$ eV for a-SiO_2. (In a recent review of the acoustic properties of glasses, Ber-

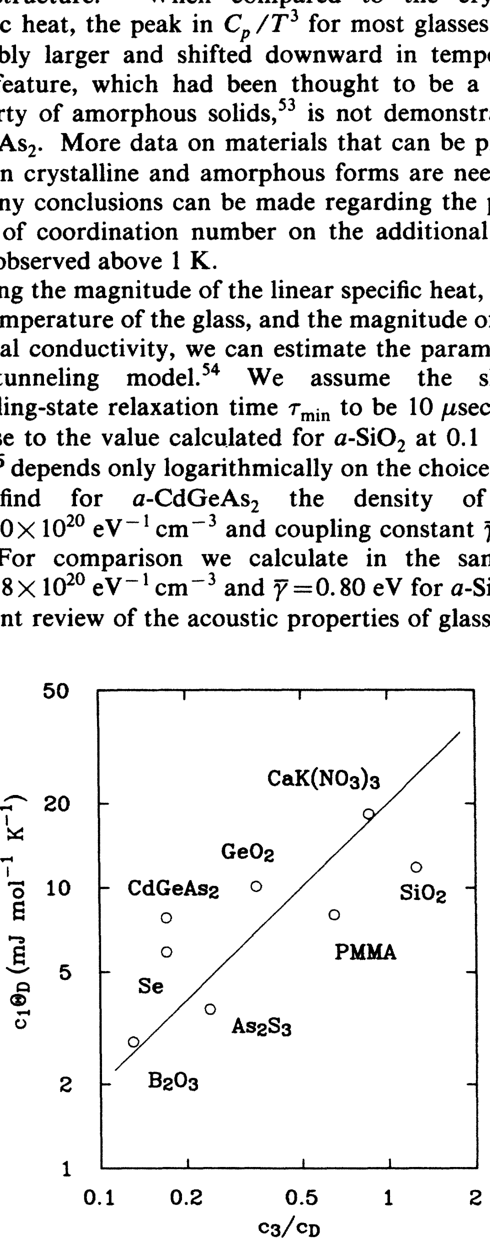

FIG. 8. Excess specific heat in amorphous solids. We attempt to correlate the low-temperature excess specific heat measured by the linear term c_1 with the excess T^3 specific heat c_3T^3 that is important above 1 K. The linear term is evaluated at the Debye temperature Θ_D. The excess T^3 specific heat is scaled by the Debye prediction c_DT^3 to give a dimensionless ratio. $CdGeAs_2$ point from this work as in Fig. 6; all other data are from Ref. 28.

ret and Meissner[56] find for a-SiO$_2$ $\bar{P}=1.3\times10^{20}$ eV^{-1}cm^{-3} and $\bar{\gamma}=0.73$ eV.)

We have observed that the specific heat and thermal conductivity of a-CdGeAs$_2$ give strong evidence for the existence of tunneling states in this material. We do not, however, see how current models assuming individual atomic motion as the cause of the tunneling states can be applied to the highly constrained structure of this glass. The possibility that the tunneling states arise from impurities or defects in an otherwise Debye-like solid cannot be ruled out but the similar magnitudes of $\bar{P}$ and $\bar{\gamma}$ for all amorphous solids casts doubt on this picture. Also, since the density of the glass is larger than that of the crystal, free-volume models seem inapplicable.[57]

We speculate that the tunneling states are a direct consequence of the vibrational states of a highly disordered solid. Buchenau *et al.*[58] have suggested that the tunneling states result from the low-frequency end of the distribution of vibrational states they observed in neutron-scattering experiments on a-SiO$_2$. In Fig. 8 we attempt to draw a correlation between the excess T^3 specific heat and the linear specific heat observed below 1 K using data from this work and data from the literature.[28] The linear term is evaluated at the Debye temperature and the excess T^3 specific heat c_3T^3 is divided by the Debye specific heat c_DT^3 predicted from the speeds of sound. The fit to a linear dependence is surprisingly good considering the wide variety of structures and chemical bonding represented here. At least when scaled in this way, the size of the linear and excess T^3 anomalies appear to be directly related.

V. CONCLUSIONS

Through measurements of the thermal properties, we have shown that a-CdGeAs$_2$ is a typical glass. We find evidence for tunneling states in both the thermal conductivity and specific heat below 1 K. The density of states and coupling strength to phonons of the tunneling states are comparable to what is observed in all other amorphous solids despite its tetrahedral coordination.

When scaled by the Debye prediction, the specific heat above 1 K of amorphous and crystalline CdGeAs$_2$ are very similar. This comparison of glass and crystal was not previously possible for a tetrahedrally bonded solid due to the difficulty in obtaining reliable speeds of sound in thin films of a-Si and a-Ge.

The thermal conductivity of a-CdGeAs$_2$ closely resembles the data for a-Ge above 30 K where the thermal conductivity is insensitive to the morphology of the thin films, and also below 10 K when compared to data on high-density films. The data show the onset of very strong phonon scattering at 5 K that leads to the minimum thermal conductivity at room temperature.

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