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Thermal conductivity of amorphous and crystalline Ge and GeTe films

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The thermal conductivity of 2000–9000-Å-thick amorphous and crystalline films of Ge and GeTe has been measured in the temperature range 100–550 °K. No thickness dependence has been observed in these films down to 2000 Å. The results show that crystalline Ge and amorphous Ge and GeTe films have a negligible electronic contribution in the measured thermal conductivity. However, as expected, crystalline GeTe films exhibit significant electronic contribution which is ~25% of the measured value of the thermal conductivity. The thermal conductivity of both amorphous Ge and GeTe increases slowly with increasing temperature in contrast to the rapid decrease in the crystalline films. In the latter case, the lattice component of the thermal conductivity decreases approximately inversely with temperature. The observed temperature dependence of the thermal conductivity can be understood on the basis of a combination of (i) umklapp-scattering mechanism, (ii) scattering due to defects, and (iii) scattering by grain boundaries. The last term, which is primarily responsible for the observed thermal resistance in the case of amorphous films, leads to a temperature-independent phonon mean free path. The observed increase of thermal conductivity with temperature for amorphous films is, therefore, attributed to the increase of specific heat with temperature. The values of the phonon mean free path in amorphous films as deduced from the thermal-conductivity data are ~3 Å in amorphous GeTe and ~5 Å in amorphous Ge films. These values suggest a relatively longer short-range order (coherently scattering regions) in amorphous Ge, as compared with amorphous GeTe.

I. INTRODUCTION

Amorphous semiconductors have recently attracted a great deal of attention from both theoretical and experimental investigators.[1] The major purpose of these investigations is to understand the effect of the loss of long- and short-range order characteristic of a crystalline material on such fundamental properties as energy-band structure (and related problems) and transport processes. Such understanding is expected to be revealed by a comprehensive study of structural, electrical, optical, and thermal properties of suitable materials which exist in both crystalline and amorphous phases. Although numerous physical properties of such materials in thin-film form have been studied, very little is known about their thermal properties.

Among the various thermal-transport parameters, specific heat and thermal conductivity are of considerable fundamental and technical interest. If specific heat is due only to the vibrational modes corresponding closely to those of a fully excited harmonic oscillator, both amorphous and crystalline structures of the same material are expected to have the same value and temperature dependence of the specific heat. This is borne out by limited studies on bulk glasses. For example, the specific heat is the same for liquid, glass, and crystalline phases of $Ge_{83}Te_{17}$.[2] A slightly higher specific heat has been observed[3] in amorphous Ge films as compared with crystalline Ge. This has been attributed to the existence of broken bonds. In contrast to the behavior of specific heat, thermal conductivity, which is directly related to the fundamental parameter of mean free path (mfp) of heat carriers, is expected to be considerably influenced by the lack of long-range order in an amorphous material. This is so because the phonon mfp is now expected to be limited by the extent of the prevailing short-range order which would be of atomic dimensions and will be independent of temperature. This conclusion has indeed been supported by the measured thermal-conductivity behavior of bulk amorphous Se[4] and $CdGeAs_2$.[5] There exist no such studies on amorphous semiconductor films primarily because of the experimental difficulty in measuring thermal conductivity of films. The present authors have developed[6] two techniques to measure the thermal conductivity of films at low and high temperatures. These techniques have been employed in the present investigations to study the temperature dependence of the thermal conductivity of amorphous versus crystalline Ge and GeTe films and thereby to deduce information on the phonon mfp and the microstructure (coherently scattering microscopic regions). Our choice of Ge and GeTe is dictated by the following factors: (i) The structural, electrical, and optical behavior of both crystalline and amorphous phases of Ge and GeTe films have been studied extensively. (ii) Whereas the short-range order of the amorphous and crystalline phases of Ge is same, the two are drastically different in GeTe films. (iii) As compared with little or no dependence of the properties of amorphous GeTe films on the deposition parameters, the properties of Ge films are extremely sensitive, most likely as a result of microscopic structural rearrangement. (iv) There continues to exist some controversy[7] regarding the possible existence of an ordered micropolycrystalline region ~14 Å in amorphous Ge films.

II. EXPERIMENTAL DETAILS

Amorphous Ge and GeTe films were prepared by thermal evaporation of high-purity Ge and GeTe (obtained by alloying Ge and Te in an evacuated quartz ampoule) from a tungsten basket onto substrates maintained at room temperature in a vacuum ~5×10^{-6} Torr. Crystalline films of Ge and GeTe were prepared by depositing onto heated substrates; the substrate temperature was maintained at 700 °K for Ge films and 420 °K for GeTe films. Substrates of freshly cleaved mica (< 0.1 mm thick) were used in all the investigations. A large distance between the substrate and the source was maintained to ensure uniformity of the film thickness over the whole substrate area. The thickness of the films was measured both gravimetrically (by a microbalance) and interferometrically.

Electron microscopy studies were conducted to ascertain whether the films are amorphous or polycrystalline in nature. Both Ge and GeTe films deposited onto substrates maintained at room temperature exhibited halotype electron diffraction patterns indicating an amorphouslike structure. Films deposited at temperatures higher than 420 °K in the case of GeTe and 700 °K in the case of Ge exhibited electron diffraction patterns characteristic of the corresponding crystalline materials.

Thermal conductivity of the films in the temperature range 100–500 °K was measured by the techniques described in an earlier paper.[6] The steady-state technique used for measurements above room temperature essentially consisted of heating one end of a bare substrate and a coated substrate. Heat sinks were attached to the other end of these substrates. Measuring the temperature of the sinks under steady-state conditions and using the mathematical formulation described in the earlier paper, the thermal-conductivity values were obtained. The transient technique used for measurements below and above room temperature consisted of recording as a function of time the temperatures of the sinks attached to one end of a bare substrate and a coated substrate while the other ends were being heated or cooled. Both techniques yielded nearly the same results. Along with thermal-conductivity measurements, the electrical resistivity of the films was also measured using a Keithley electrometer (model No. 610C).

III. RESULTS AND DISCUSSION

Figure 1 shows the thickness dependence of the thermal conductivity of amorphous and crystalline Ge films of thicknesses between 2000–10 000 Å at 338 °K. Similar results are obtained for GeTe films. As expected, the thermal conductivity of both amorphous and crystalline films does not show any thickness (size) dependence because of the small values of the phonon mfp (~5 Å in amorphous Ge and GeTe and ~20 Å in crystalline Ge and GeTe films). As we shall see later, the thermal conduction is mainly by phonons in all the cases except for crystalline GeTe films. In the case of crystalline GeTe films, there is some electronic conduction (as discussed later) but, due to the small mfp of the holes, size effects are expected to be negligible for thicknesses > 500 Å.

Figures 2 and 3 show the temperature dependence of the thermal conductivity of amorphous and crystalline Ge and GeTe films, respectively. Also shown in Fig. 3 is the electrical resistivity of a crystalline GeTe film. The room-temperature values of the electrical resistivities of Ge and GeTe films prepared under different conditions are listed in Table I.

The two distinct thermal-conductivity mechanisms operative in a semiconductor are (i) Conduction via electron diffusion, and (ii) conduction via longitudinal and transverse elastic waves. One can write the total thermal conductivity as

$$K = K_L + K_e , \qquad (1)$$

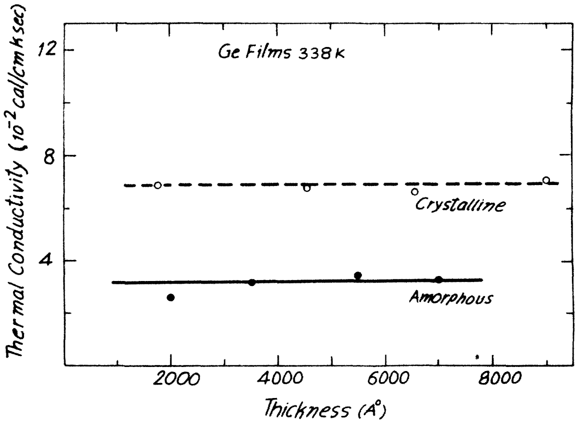

FIG. 1. Thermal conductivity vs thickness at 338 °K for amorphous and crystalline Ge films.

where K_L is the lattice thermal conductivity in the absence of electronic conduction and K_e is the thermal conductivity due to electrons and holes. The electronic contribution to thermal conductivity can be calculated using the Wiedemann-Franz law

$$K_e = A\sigma(k/e)^2 T, \tag{2}$$

where k is the Boltzmann constant, e is the electronic charge, T is the absolute temperature and σ is the electrical conductivity. A is a constant equal to 2 in nondegenerate electron system and A is equal to $\frac{1}{3}\pi^2$ for a degenerate system (for example, crystalline Ge and GeTe films).

It has been established by the study of various workers[8] that crystalline GeTe is a p-type degenerate, narrow-band-gap semiconductor with a hole concentration of $\sim 10^{20}$ cm^{-3}. Also, evaporated crystalline Ge films behave[9] like a p-type degenerate semiconductor with a carrier concentration $\sim 10^{18}$ cm^{-3}, irrespective of the purity of the starting material. The use of the Wiedemann-Franz relation to estimate the electronic component of the thermal conductivity shows that amorphous Ge and GeTe and crystalline Ge films have a negligible electronic component in the whole region of temperature investigated by the authors. Although crystalline Ge films are also degenerate, the electronic component of the thermal conductivity is negligible because of the smaller carrier concentration and their mobility.

As expected, degenerate crystalline GeTe films exhibit electronic contribution to thermal conductivity. The electrical resistivity of crystalline GeTe films increases with temperature (Fig. 3). Below 300 °K, the variation is nearly linear. At temperatures above 300 °K, the electrical resistivity rises rapidly as a power of temperature. The temperature coefficient of resistivity of GeTe depends[8] on the hole concentration which in turn depends on the deposition temperature of the film. The temperature variation of the electronic contribution, K_e, obtained from the Wiedemann-Franz law for crystalline GeTe films is shown in Fig. 3. It is seen that K_e increases linearly with temperature up to nearly 350 °K and then becomes nearly constant. K_e at room temperature is nearly 25% of the observed total thermal conductivity.

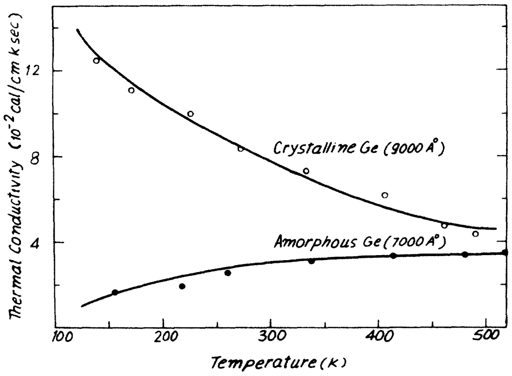

FIG. 2. Thermal conductivity vs temperature for amorphous and crystalline Ge films.

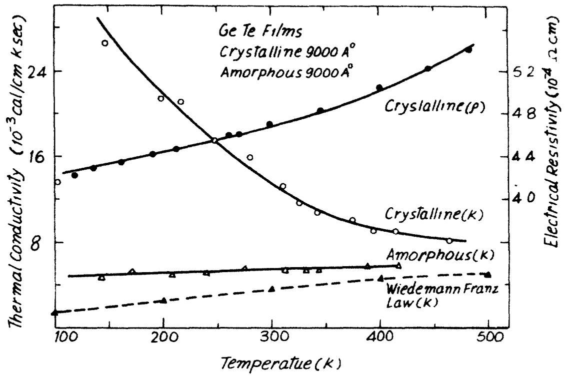

FIG. 3. Thermal conductivity vs temperature for amorphous and crystalline GeTe films. Also shown is the variation of the electrical resistivity with temperature and the variation of the electronic part of the thermal conductivity with temperature for a crystalline GeTe film (9000 Å), deposited at 420 °K.

As noted in the preceding discussion, the thermal conduction in crystalline Ge films is completely by lattice waves. The lattice component of the thermal conductivity in crystalline GeTe films can be obtained by subtracting the electronic component from the measured values. The lattice part of the thermal resistivity may arise because of (i) the umklapp process, (ii) scattering by impurities and lattice imperfections, and (iii) scattering by the grain boundaries. If all the contributions are considered to be independent, one can write

$$1/K_L = 1/K_u + 1/K_d + 1/K_b . \tag{3}$$

The first term in the equation arising from phonon-phonon scattering (umklapp processes) is given by

TABLE I.

Material	Thickness (Å)	Electrical resistivity (Ω cm)
Amorphous Ge	7000	10^2–10^3
Crystalline Ge	9000	2×10^{-1}
Amorphous GeTe	9000	10^2–10^3
Crystalline GeTe	9000	4.78×10^{-4}

an equation of the form

$$1/K_u = AT^m e^{-\Theta/2T}, \tag{4}$$

where A is a constant and Θ is the Debye temperature. For $T \ll \Theta$, m lies between 1 and 2. For $T > \Theta$, this equation reduces to

$$1/K_u \propto T/\Theta . \tag{5}$$

The thermal conductivity below the Debye temperature rises more rapidly than described by Eq. (5). However, a negligible departure from the $1/T$ law even below the Debye temperature is observed in many cases.[10] Also, for some materials, the thermal resistivity above the Debye temperature does not show the temperature dependence of Eq. (5) because of the occurrence of the four-phonon processes; this results in a higher temperature dependence.

The second term in Eq. (1) arises because of scattering by impurities and defects. Thin films are, in general, known to have a high concentration of defects and these are likely to produce a significant contribution towards the thermal resistivity. The smaller the ratio of the phonon wavelength to the size of defects, the greater is the scattering. At temperatures well below Θ the predominant phonons have wavelength that exceed the dimensions of atoms and lattice defects so that phonons are scattered only slightly. Phonons of shorter wavelength become dominant as the temperature rises and these are scattered more strongly. Therefore, the resistance caused by defects and impurities increases with temperature. This contribution can be described by

$$1/K_d = BT^{p-x} . \tag{6}$$

Here $p \sim 1$; for $T > \Theta$, $x = 0$; for $T \ll \Theta$, $x = 3$. The factor x takes into account the variation of the specific heat with temperature.

The third term of Eq. (3) arises because of scattering of phonons at grain boundaries or film surfaces. This term plays the most important role in the case of amorphous films. In fact, the whole of the contribution towards thermal resistivity is due to this type of scattering.

The data for crystalline Ge films when replotted in the K^{-1} vs T form (Fig. 4) show that beyond 300 °K the thermal conductivity varies as $1/T$. Below 300 °K, the K^{-1}-vs-T curve starts deviating from the straight-line behavior. The thermal resistance arising from the umklapp processes should show a $1/T$ dependence down to a much lower temperatures in the case of Ge. It has been observed by various workers[10] that, in the case of bulk Ge, there is no region of temperature in which the lattice thermal conductivity varies exponentially with the inverse of temperature as expected on the basis of Eq. (4). Carruthers *et al.*[11] attribute this behavior to the scattering by isotopes of Ge. Geballe and Hull,[12] however, conclude from their neutron-diffraction experiment that the maximum energy of the transverse acoustical branch of the vibration spectra of Ge is about 7×10^{-3} eV. As a result, the umklapp scattering associated with phonons in this branch persists to a much lower temperature than would have been expected on the basis of the normal Debye temperature of 372 °K (obtained from the specific-heat data) which corresponds to $k\Theta = 3.2\times10^{-2}$ eV. This interpretation would suggest that Ge behaves as if it had a Debye temperature of only 80 °K. Theoretical analysis is available in the literature[10] which can be used to calculate this part of the thermal resistance. For Ge one obtains $K_u T \simeq 36$ cal/cm sec. From our general electron microscopy studies of Ge films, we know that the grain size in crystalline Ge films is > 100 Å which is significantly larger than the estimated phonon mfp (discussed later). Therefore, the contribution to thermal resistance due to the grain boundaries and film surfaces in thick (~5000 Å) film is expected to be small, i.e., $K_b \simeq 0$. Using the measured values of the thermal conductivity, one can thus obtain the approximate contribution due to defects and impurities. The plot of K_d^{-1} vs T (calculated by subtracting K_u^{-1} from K^{-1}) is given in Fig. 4. It is seen that for $T > 300$ °K, K_d^{-1} varies as T. As the temperature is lowered, the specific-heat term in Eq. (6) starts dominating. It is this deviation which is responsible for the deviation observed in K^{-1} vs T at low temperatures.

The interpretation of the temperature dependence of the thermal conductivity of crystalline GeTe film should be quite simple as we are working in the region of temperature which is above the Debye temperature of GeTe (130 °K as obtained from Lindeman melting-point rule). The lattice

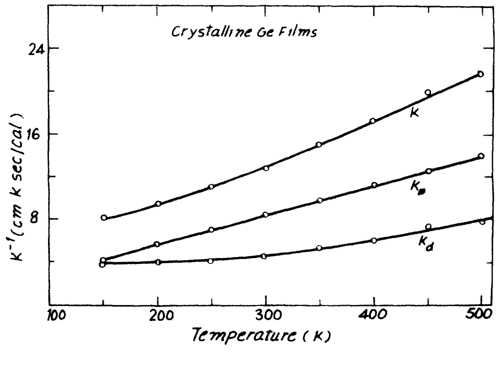

FIG. 4. K^{-1}-vs-T plots for Ge films.

thermal conductivity as obtained by subtracting the electronic component shows a temperature dependence of the form $K_L \propto T^{-n}$ ($n = 1.5-1.7$). This is in contrast to the T^{-1} dependence expected on the basis of Eq. (5). However, a similar temperature dependence has also been observed in other semiconductors.[10]

Krestonikov *et al.*[13] have measured the thermal conductivity of bulk GeTe. They obtained a value of $K_L = 1.13\times 10^{-2}$ cal/cm sec °K at 273 °K. The value of K_L at 273 °K as obtained from our data is $\sim 1.04\times 10^{-2}$ cal/cm °K. However, Krestonikov *et al.* obtained a high value of $\sim 9.5\times 10^{-3}$ cal/cm sec°K for the electronic component of the thermal conductivity whereas our value is $\sim 3.7\times 10^{-3}$ cal/cm sec°K. This difference in the values of electronic component of thermal conductivity can be attributed to the difference in the concentration of holes in GeTe. It has been established by the studies of Bahl and Chopra[8] that the electrical resistivity which in turn determines the hole concentration of crystalline GeTe films decreases with increasing deposition temperature. For a substrate temperature of ~600°K, the values of the electrical resistivity and its temperature dependence are quite close to those observed for bulk GeTe.

Keyes's[14] formulas based on Lindeman's melting-point rule can be used to predict the lattice part of the thermal conductivity (that part arising from umklapp process only) as

$$K_u T = B T_m^{3/2} d^{2/3} A^{-7/6}, \qquad (7)$$

where B is a constant, T_m is the melting point, d is the density, and A is the mean atomic weight. Keyes argued that the value of B does not vary from one solid to another provided the two have a similar type of binding. The value of B which gives the best fit for various semiconductors is 0.06. This value of B yields $K_u T = 6$ cal/cm sec. The value of $K_L T$ obtained from the experimental data of GeTe films is ~ 3 cal/cm sec. Note that the measured value of K_L includes the contribution due to defects and impurities whereas the value of $K_u T$ obtained from Keyes's relation includes only the contribution due to the umklapp process. The observed difference could be due to two factors. One is that the film contains a large number of defects which contribute significantly towards thermal resistivity. Indeed, studies[8] of the various properties of GeTe show that crystalline GeTe must have as many as 2-at.% Ge vacancies. The second factor is the value of the constant B. A value of B which gives a best fit for various semiconductors has been used. The binding in GeTe is known to be a mixture of covalent and ionic binding. For covalent crystals, the value of B is 0.13 and for ionic crystals the value of B that gives best results is 0.015. The exact value of B for a material like GeTe which exhibits mixed binding is difficult to estimate. Thus Keyes's relation can be used to predict only qualitatively the significant role of structural defects.

Thermal conductivity of both amorphous Ge and GeTe increases slowly with temperature (Figs. 2 and 3). The increase for Ge films is, however, more compared to GeTe films. This is expected because in the case of GeTe, the region of temperature is above the Debye temperature. In this region of temperature, the specific heat increases only slightly with temperature. The thermal conductivity of GeTe over the whole temperature region can be described by an empirical relation of the form

$$K_{\text{amor}}(\text{GeTe}) = 4\times 10^{-6} T \text{ cal/cm sec °K}. \qquad (8)$$

The case of amorphous Ge is different. Above the Debye temperature (372°K), the thermal conductivity increases linearly with temperature and is given by

$$K_{\text{amor}}(\text{Ge}) = 1.7\times 10^{-4} T \text{ cal/cm sec°K} \quad (\text{for } T > \Theta). \qquad (9)$$

Below the Debye temperature, the thermal conductivity falls more rapidly and this fall is governed by the specific heat of Ge. Note that the temperature variation of the thermal conductivity of both amorphous Ge and GeTe films is very similar to that observed for amorphous bulk Se,[4] Cd GeAs$_2$, and As$_2$Se$_3$.[5]

By assuming a Debye spectrum for phonons and thus neglecting dispersion and anisotropy effects, and by ignoring the distinction between longitudinal and transverse phonon branches, (by using an average group velocity) we can calculate the mfp of phonons in crystalline and amorphous films. The thermal resistance arising as a result of multiple scattering of randomly moving phonons is analogous to diffusion or thermal conduction in gases and can be described by an equation of the form

$$K_L = \tfrac{1}{3} C_v v l, \qquad (10)$$

where v is the average speed of a phonon (that is, the average speed of propagation of elastic waves), C_v is the specific heat per unit volume of the lattice, and l is the mfp of phonons.

The value of C_v is given quite accurately by the Debye theory of specific heat as

$$C_v = 3Rf(\Theta_T). \qquad (11)$$

The specific heat of Ge and GeTe was calculated using this expression. The values of $f(\Theta/T)$ are available in the literature.[15] The value of v was calculated using the expression for the average group velocity

$$v = (k/\hbar)(6\pi^2)^{-1/3}\Theta\gamma , \qquad (12)$$

where k is the Boltzmann constant, $\hbar = h/2\pi$ with h is Plank's constant, Θ is the Debye temperature, and γ is the cube root of atomic volume. Although the density of amorphous GeTe differs from crystalline GeTe by nearly 10%, the velocity of phonons will be different by only ~2%. The above expression yields $v \simeq 1.0\times 10^{-5}$ cm/sec for GeTe and ~3×10^5 cm/sec for Ge. The velocity v is assumed to be independent of temperature. The value of Θ used in the above expression is calculated by using the Lindeman melting-point rule which yields $\Theta = 372\,^\circ$K for Ge and $\Theta = 130\,^\circ$K for GeTe.

The values of the phonon mfp as obtained by the preceding analysis are shown in Fig. 5. For both crystalline Ge and GeTe films, the phonon mfp has nearly $1/T$ dependence, as expected. The phonon mfp for both amorphous Ge and GeTe is independent of temperature. In the case of amorphous GeTe, the value of the phonon mfp is ~2.8 Å. This value of phonon free path matches well with the dimensions of a GeTe unit cell ~Å. As suggested by Kittel,[16] the phonon mfp in an ideal amorphous material should be equal to dimensions of the smallest coherent scattering region. The closeness of the calculated mfp and the size of the GeTe unit cell confirms the studies of various workers on amorphous GeTe films[1] in that GeTe is an ideal amorphous semiconductor in which the short-range order is limited to the first nearest neighbors and it is different from the corresponding crystalline phase. In the case of amorphous Ge, it has been well established[1] that the short-range order in both the crystalline and amorphous phases is the same. The value of the phonon free path calculated from our measurements of the thermal conductivity of amorphous Ge is about 5 Å. Radial distribution function (RDF) studies[1] have shown that the radius of the first coordination sphere is ~2.5 Å which is nearly the same as that for the crystalline phase. The second coordination sphere of radius 4 Å is also the same for both phases of Ge. Thereafter, significant differences exist between the RDF's of the amorphous and crystalline phases of Ge. Our calculated value of the phonon free path suggests that the size of the basic scattering unit in amorphous Ge is ~5 Å. Although not much significance can be attached to this value, it being higher than for GeTe does suggest that the short-range order in Ge is more extended than in GeTe.

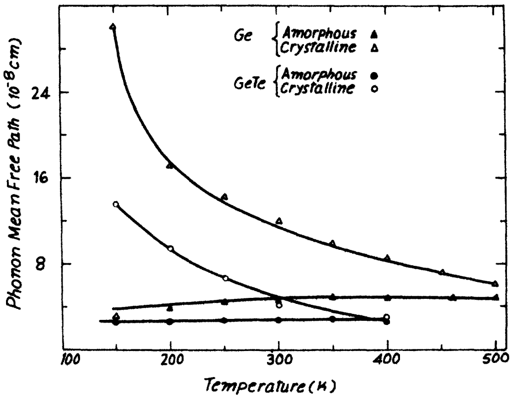

FIG. 5. Variation of the phonon mfp with temperature for crystalline and amorphous Ge and GeTe films.

IV. CONCLUSIONS

The electronic contribution to the measured thermal conductivity is negligible in the case of degenerate crystalline Ge films and is about 25% in degenerate crystalline GeTe films. The lattice component of the measured thermal conductivity varies with temperature in the expected way.

Thermal conductivity of amorphous Ge and GeTe films is entirely due to the lattice contribution. Its temperature variation can be understood in terms of the temperature dependence of the corresponding specific heat.

The larger value (~5 Å) of the grain size limited phonon mfp for amorphous Ge as compared with ~3 Å for GeTe strongly suggests that the short-range order is relatively more extended in Ge than in GeTe.

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