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THE EFFECT OF MICROSTRUCTURE ON THE THERMAL CONDUCTIVITY OF PARTICULATE ZnS/DIAMOND COMPOSITES

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ABSTRACT

We have observed that the thermal conductivity of zinc-sulphide is increased by adding large particles of highly conducting diamond, but lowered by the addition of sub-micron size particles of diamond. This effect is explained in terms of the interfacial thermal resistance which becomes increasingly dominant as the particles become smaller (because that increases their surface to volume ratio). A phenomenological model in which the interface resistance is expressed as an effective Kapitza radius, a_K, is presented. The conductivity of the composite is analyzed for different values of α, which is defined to be equal to the Kapitza radius divided by the particle radius. If $\alpha=1$, that is, the actual particle radius is equal to a_K then the effective thermal conductivity of the particles is equal to that of the matrix. If $\alpha>1$, that is the particles are very small, then the contribution of the particles to the thermal conductivity of the composite is dominated by interfaces; if $\alpha<1$ then the bulk property of the particles is important. Our measurements yield $a_K \approx 1.5$ μm for the ZnS-Diamond interface.

1. INTRODUCTION

Most fundamental experimental studies of thermal boundary resistance have been carried out on planar interfaces. The purpose of this paper is to demonstrate that measurements of the thermal conductivity of particulate composites provide an alternative simple means of obtaining information on thermal boundary resistance. The (specific) boundary resistance, R_{Bd}, is defined in terms of the heat flux, $\dot{Q}$, and the consequent temperature discontinuity, ΔT, across the interface by the equation:

$$\dot{Q} = \frac{\Delta T}{R_{Bd}} . \tag{1}$$

The first measurements of thermal boundary resistance were carried out by Kapitza [1] in 1941; his experiments on metal-liquid helium interfaces, now known as a Kapitza boundary, have become the basis for the theoretical development of R_{Bd}. The solid-liquid interface studied by Kapitza is still an important point of reference because in contrast to solid-solid interfaces, the solid-liquid interfaces are expected to be atomically sharp and free of local damage.

An up to date review of theoretical models for R_{Bd} is given in a recent article by Swartz and Pohl [2] who also present results from careful experiments on the thermal resistance of solid-solid, metal-ceramic interfaces. The mechanisms of thermal conduction across interfaces are revealed by measuring the resistance as function of temperature, starting from temperatures well below the Debye temperature of either of the constituents that form the interface. The thermal resistance is observed to decrease as T^{-3} up to a temperature somewhat below the lower of the Debye temperatures of the two materials, and then become relatively temperature independent. The model usually put forward

to explain this behavior is the acoustic mismatch model. In this model the propagation of a phonon across an interface is treated in terms of an acoustic wave that is refracted at the interface subject to boundary conditions of continuity of displacement and traction force. A modification of the acoustic mismatch model is the diffuse scattering model, in which all phonons arriving at the interface are randomly scattered, the number of them going to one side or the other depending on the density of states available to them in the two materials.

In the case of solid-solid interfaces, such as Rh:Fe/Al_2O_3 [2], where the Debye temperatures of the two consitutents differ widely, the models give excellent agreement in the long wavelength limit when the temperature is below the Debye temperature of the metal, but underestimate R_{Bd} by nearly an order of magnitude above this temperature. This discrepancy has been explained in terms of the structural features of the interface. In the ZnS/D system we find a similar discrepancy between theory and experiment at room temperature, which lies close to the Debye temperature for ZnS but below that of diamond.

In this paper we draw a link between simple experiments with planar geometries of interfaces and experiments with particulate composites where interfaces are distributed in different configurations depending on the microstructure. We put forward a model that relates R_{Bd} to the measurement of the average thermal conductivity of the composite where particles of one material are evenly dispersed in the matrix of the other. In this geometry the thermal conductivity of the composite becomes dependent on the particle size (diameter) of the dispersed phase if boundary resistance is high (because the surface to volume ratio of the particles increases with smaller particles). We account for this microstructure by defining a non-dimensional parameter, α, as follows:

$$\alpha = a_K/a. \qquad (2)$$

Here a is the radius of the dispersed particles, and a_K is the Kapitza radius defined as:

$$a_K = R_{Bd} K_m, \tag{3}$$

where K_m is the thermal conductivity of the matrix.

Before proceeding to describe the model where the thermal conductivity of the composite is analyzed in terms of α and the volume fraction of the dispersed phase, it is illuminating to note a physical interpretation for a_K in terms of the acoustic mismatch theory. A simple Debye model for R_{Bd} [2] yields:

$$R_{Bd} = \frac{4}{\rho C v \eta}, \tag{4}$$

where ρ is the density, C the specific heat and v the Debye velocity of the matrix and η is the average probability for the transmission of the phonons across the interface into the particles. On the same level of approximation the thermal conductivity K_m is often expressed as:

$$K_m = \frac{1}{3} \rho C v \ell \tag{5}$$

where ℓ is the phonon mean free path. Combining Eqns (3), (4) and (5) one obtains:

$$a_K \approx \ell / \eta \ . \tag{6}$$

Thus, the Kapitza radius is greater that the mean free path of phonons in the matrix by a factor that is equal to the inverse of the probability with which the phonons can be transmitted across the interface or, loosely speaking the number of attempts before a phonon is succesful in crossing the interface. A low probability will, therefore, lead to a large a_K, and from Eq (2), to a large α.

2. EFFECTIVE MEDIA THEORY FOR THE THERMAL CONDUCTIVITY OF A PARTICULATE COMPOSITE

2a. Low Volume Fraction Limit

Theories for the transport properties of composite media date back to the early investigations of Maxwell [3,4], whose analysis applies when the second phase is dispersed in small volume fractions. The effect of the thermal boundary resistance on the effective conductivity of the composite has also been recognized for some time [5,6,7] but Maxwell's theory has been modified to include this effect only recently by Hasselman and Johnson [8] and Benveniste [9]. They consider a dispersal of spherical particles of radius a, of a material having a thermal conductivity K_d, occupying a volume fraction f, embedded in a matrix of conductivity K_m. Their results for the effective conductivity of the composite, K_c, can be written in the following form:

$$\frac{K_c}{K_m} = \frac{[K_d(1-2\alpha)-2K_m]-2f[K_d(1-\alpha)-K_m]}{[K_d(1+2\alpha)-2K_m]-f[K_d(1-\alpha)-K_m]} \quad . \tag{7}$$

In the limit of small f, where Maxwell model is most appropriate, this equation reduces to:

$$\frac{K_c}{K_m} = 1 - 3f\,\frac{[K_d(1-\alpha)-K_m]}{[K_d(1-2\alpha)-2K_m]} \, . \tag{8}$$

Other interesting limits of Eq. (7) obtain when we consider a composite where the intrinsic conductivity of the dispersed phase is much greater than that of the matrix, as in the case of the ZnS/D composite. Then, substituting $(K_d/K_m) \gg 1$ into Eq. (7) we obtain that:

$$\frac{K_c}{K_m} = \frac{1-2f(1-\alpha)/(1-2\alpha)}{1-f(1-\alpha)/(1-2\alpha)} \quad . \tag{9}$$

Equation (9) further simplifies for limiting values of α. When the interface resistance is very high, we get:

$$\frac{K_c}{K_m} = \frac{1-f}{1+0.5f} \quad , \alpha \to \infty \tag{10}$$

and when the interface resistance is negligible, Eq. (9) reduces to:

$$\frac{K_c}{K_m} = \frac{1-2f}{1-f} \quad , \alpha \to 0 \tag{11}$$

Next we consider Bruggeman theory for high volume fraction composites.

2b. High Volume Fraction Limit

An accurate calculation of the conductivity at high concentrations would require extensive information about the correlations between the positions of the particles and about their multipolar polarizabilities etc. [10,4]. This is a formidable problem and as an interim measure an approach along the lines of Bruggeman effective medium theory offers a simple method of estimating the effects of these interactions.

Bruggeman theory proceeds from the premise that the fields of neighboring particles can be taken into account by adding the dispersed particles incrementally, taking the surrounding medium to be the existing composite at each stage. Equation (8) is cast in the differential form

$$dK = 3K \frac{df'}{(1-f')} \frac{\left|K_d(1-\alpha)-K\right|}{\left|K_d(1-2\alpha)-2K\right|} \tag{12}$$

for this purpose. On integrating K between the limits K_m and K_c and f' between 0 and f one obtains

$$(1-f)^3 = \left\{\frac{K_m}{K_c}\right\}^{(1+2\alpha)/(1-\alpha)} \times \left\{\frac{K_c-K_d(1-\alpha)}{K_m-K_d(1-\alpha)}\right\}^{3/(1-\alpha)} , \tag{13}$$

A distribution of particle sizes can be accommodated by treating α in Eq. (12) as a function of f'. A number of limiting cases are of interest. The result

$$(1-f)^3 = \frac{K_m}{K_c}\left\{\frac{K_c-K_d}{K_m-K_d}\right\}^3 , \qquad (14)$$

is obtained by setting $\alpha \rightarrow o$, which applies in the limit wnere the particles are much larger than the Kapitza radius or the interface resistance vanishes. The opposite limit, $\alpha \rightarrow \infty$, for particles small compared to a_K or large interface resistance, yields

$$(1-f)^3 = \left\{\frac{K_c}{K_m}\right\}^2 . \qquad (15)$$

Equations (14) and (15) correspond to the ordinary results of the Bruggeman theory without consideration to the interface resistance. Equation (14) is the general Bruggeman result, while Eq. (15) holds for insulating particles.

In the context of ZnS/D composites it is interesting to consider the limit for Eq. (13) when $(K_d/K_m) \gg 1$, that is when the dispersed phase is much more conducting than the matrix. Then, we obtain the following result:

$$\frac{K_c}{K_m} = \frac{1}{(1-f)^{3(1-\alpha)/(1+2\alpha)}} . \qquad (16)$$

Plots of Eqns (9) and (16) are given in Fig 1(a) and (b). They show the effect of the particle radius and the interface resistance R_{Bd}, on the thermal conductivity of the composite, both these effects having been normalized into one parameter $\alpha = a_K/a$, where the Kapitza radius a_K is proportional to R_{Bd}. Both results, Maxwell and Bruggeman, predict that the effective thermal conductivity of the composite will be unchanged by the particles if $\alpha = 1$, that is, if the radius of the dispersed particles is the same as the Kapitza radius. The contribution of the interface resistance is then exactly balanced by the higher thermal conductivity of the particles. If the particles are smaller than the Kapitza radius, the

effective conductivity of the composite is lowered by the particles even if the particles themselves have a higher conductivity than that of the matrix. Thus the Kapitza radius becomes a physically important parameter in the design of composites where the objective is to change the thermal conductivity by mixing two different constituents. The equations here can also be used to measure the Kapitza radius from particulate composites through the determination of α. That then leads to the estimate of R_{bd}, through Eq. (3), which is a result that can be related to the traditional method of using planar, semi-infinite geometries for determining the interface resistance.

The plots in Fig. 1 show that the insulating limit, that is when the particles are very small is nearly realized when the particle radius is one seventh of the Kapitza radius, and the conducting limit reached when the particles are about ten times the Kapitza radius. Thus for example, if the Kapitza radius for the ZnS-D interface is 1 μm (see below) then the maximum benefit of the diamond inclusions to the thermal conductivity would be obtained if the diamond particles have a radius of about 10 μm. Such guidelines can be useful in the design of composite materials.

We now proceed to present experimental results for the ZnS/D composites for two different particle size of diamond, which lie on either side of the Kapitza radius for the zinc-sulphide/diamond interface.

3. EXPERIMENTS

Diamond has the highest known thermal conductivity of all materials [12], exceeding 2000 W m^{-1} K^{-1} in very pure specimens. Enrichment with ^{12}C isotope has been found to increase its conductivity even further [13]. Even in sintered, polycrystalline diamond conductivities as high as 600 W m^{-1} K^{-1} have been realized. Diamond is, therefore, a natural constituent in the design of composites that are electrically insulating but have high

thermal conductivity. For example, thermal pastes consisting of fine diamond particles dispersed in an organic liquid have been found to have conductivities far in excess of the liquid alone [15].

We have investigated the thermal conductivity of particulate composites made from zinc-sulphide and diamond. Two types of diamond powders, one having the particle size (defined as twice the particle radius a) in the range 0.1 μm to 1.0 μm, and the other having particles in the range of 1.0 μm to 8.0 μm were used to make two sets of composites.

The composites were prepared by powder processing techniques. The powders of zinc-sulphide and diamond were intimately mixed. The mixture was then hot pressed in a mildly reducing atmosphere at a temperature that ranged from 900 to 1000°C under a pressure of 200 MPa. The details of the processing method are described in Ref. [16].

In hot pressing of ceramics porosity can be essentially removed completely because even very small pores at interfaces become filled by diffusional transport of atoms in the solid state, irrespective of the complexity of the shape of the interfaces. The measurement of the mechanical and optical properties of these composite, also reported in Ref. [16], suggest not only complete but also strong bonding at the ZnS-D interface.

The thermal transport properties of ZnS/D composites was measured at room temperature by the flash diffusivity technique [17,18], using a glass-Nd laser as the flash source and a liquid nitrogen cooled InSb detector to measure the transient temperature response of the sample. For these measurements, the specimens were in the form of approximately 10 mm diameter discs with a thickness of about 1.5 mm. In order to eliminate direct transmission of the laser pulse through the specimen, the samples were sputter coated with gold to a thickness of approximately 100 nm. In turn, the gold was lightly coated with a layer of colloidal carbon in

order to enhance the thermal coupling between the sample, laser-pulse and the detector.

The measurements of the thermal diffusivity of the two sets of composites are shown in Fig. 2. They show that the small diamond particles, having an average radius of 0.25 μm lower the thermal diffusivity, while the larger particles, having an average radius of 2 μm produce a small increase in the thermal diffusivity relative to pure zinc sulphide. (Our measurement of the thermal diffusivity of pure zinc sulphide is in agreement with the value reported by Lugueva et al.[19]). The decrease in the thermal conductivity cannot be explained in terms of cracking at the ZnS-Diamond interface due to thermal expansion mismatch, since the cracks are much more likely to form with the larger particles, which runs contrary to the measurements.

4. COMPARISON OF THEORY AND EXPERIMENT

4a. Estimate of the Kapitza Radius for The Zns-D Interface

We calculate the Kapitza radius for the ZnS-D interface, a_{ZD}, in two ways. The objective is to estimate the value of R_{Bd} for the ZnS-D interface at room temperature, which lies close to the Debye temperature for ZnS (θ_D=315 K) but is well below the Debye temperature for diamond (θ_D=2230 K).

The first method is is a semi-empirical estimate based on the acoustic mismatch theory for solid-solid interfaces in the long wavelength limit [20], which yields:

$$R_{Bd} = \frac{A}{T^3}, \tag{17}$$

where A is a constant that is determined by the acoustic properties of the two solids in contact and to a lesser extent the boundary conditions assumed. Values of A calculated by Swartz and Pohl [2] for a variety of diamond:metal contacts range between 0.006 and 0.009 K^4 m^2 W^{-1}. Whether specular or diffuse boundaries are assumed makes no more than about a 10% difference to these values.

Experimental investigations based on sapphire:metal contacts show that the predictions of the acoustic mismatch model are borne out up to about 50K. Beyond this temperature there is a levelling off of the boundary resistance [2]. This is partly because the dominant phonons are nearing the Debye cutoff in frequency and the heat capacity is approaching a limit. However, Swartz and Pohl [2] report levelling off at a higher value of the resistance than expected on this basis and they attribute this to the scattering of the higher frequency phonons by subsurface damage. On the basis of the above findings one might expect the ZnS:D room temperature boundary resistance to be of the order of $R_{Bd} \approx 0.0075/50^3 \approx 6\times10^{-8}$ m^2 K W^{-1}.

In the second method we use Eq. (4) to estimate R_{Bd}. For ZnS ρ = 4100 kg m^{-3} and C = 472 J kg^{-1} K^{-1} and since transverse phonons carry most of the heat, we will take $v = \sqrt{C_{44}/\rho} = 3300$ m s^{-1}, while for diamond ρ' = 3520 kg m^{-3} and $v' = 12800$ m s^{-1}. Only phonons incident on the interface within the critical angle θ_c from the ZnS side have the opportunity of being transmitted. These constitute a fraction q of the incident phonons given by

$$q = \frac{1}{2}\sin^2\theta_c = \frac{1}{2}(v/v')^2 = 0.033. \qquad (18)$$

The probability that a phonon incident within the critical angle will be transmitted can be estimated from [2]

$$p = \frac{4ZZ'}{(Z-Z')^2}\ , \qquad (19)$$

where $Z = \rho v = 13.5 \times 10^6$ kg m^{-2} s^{-1} is the acoustic impedance of ZnS and $Z' = \rho' v' = 45.1 \times 10^6$ kg m^{-2} s^{-1} is that of diamond, which yields $p = 0.71$. Hence $\eta = pq = 0.023$ and $R_{Bd} = 2.7 \times 10^{-8}$ m^2 K W^{-1}. This value may be considered an underestimate since it ignores the effect of velocity dispersion.

Recently Young and Maris [21] and Pettersson and Mahan [22] have carried out lattice dynamical calculations of the Kapitza resistance between fcc lattices which encompass dispersion as well as the nature of the interfacial bonding. While their results are not immediately applicable to the ZnS-D interface, they are not greatly out of line with the above estimates. These model calculations reveal that increasing the strength of the bonding between the atoms of the two lattices has a relatively small effect on the Kapitza resistance, but weakening the bonding significantly reduces the transmission of the higher frequency phonons and increases the boundary resistance.

A theoretical estimate of the Kapitza radius for the ZnS-D interface, $a_{ZD}=R_{Bd}K_n$, may be obtained by substituting the higher of the two values for R_{Bd}, i.e. $R_{Bd}=6\times10^{-8}$ m^2 K W^{-1}, and taking $K_n=17.4$ W m^{-1} K^{-1} (see below), this gives a theoretical value of 1 μm for the Kapitza radius.

4b. Experimental Estimate of the Kapitza Radius for the ZnS-D Interface

The data for the thermal diffusivity of the composites were converted to thermal conductivity using the equation that (thermal conductivity)=(thermal diffusivity x ρ x C) where ρ is the density and C is the heat capacity. The following numerical values were used for ZnS: $\rho=4100$ kg m^{-3} and $C=472$ J kg^{-1} K^{-1} at 298 K, and for diamond: $\rho=3520$ kg m^{-3} and $C=509$ J kg^{-1} K^{-1} at 298 K. The effective value of ρC for the composite was obtained using rule of mixtures, that is, $(\rho C)_{composite}=(\rho C)_{diamond}f$ +

$(\rho C)_{ZnS}(1-f)$. From the measured value of 8.9×10^{-6} m^2 s^{-1} for the diffusivity of pure ZnS one obtains $K_m(ZnS) = 17.4$ W m^{-1} K^{-1}.

The experimental measurements of the thermal conductivity of the composite, normalized with respect to the thermal conductivity of ZnS, are shown in Fig. 3. Plots of K_c/K_m for $\alpha \to \infty$ lies above the data for the small diamond particles, whereas $\alpha \approx 0.75$ provide good fit with the data for the large diamond particles. Since the average radius of the diamond particles in the $\alpha \approx 0.75$ fit was 2 μm, we estimate the experimental value of the Kapitza radius to be $a_{ZD} \approx 1.5$ μm, which is comparable to the semi-empirical theoretical estimate, derived in the previous section, of $\alpha_{ZD} \approx 1$ μm.

6. DISCUSSION

The work we have presented here seeks to bridge the gap between the fundamental measurements of thermal boundary resistance from planar geometries and the understanding of how this resistance affects the thermal conductivity of particulate composites. This link allows us to include the effect of the microstructure on the properties of composites, a need that is not fulfilled by the ordinary Maxwell and Bruggeman models. The fact that we find a reasonable agreement between the value of the Kapitza radius for the ZnS-D interface obtained from composites and the value estimated from experiments with planar geometries, gives us confidence in modified Bruggeman model developed in this paper.

We now return to a result in Fig. 3 showing that the experimental measurements of thermal conductivity of the composite lie below the limit of completely insulating interfaces, that is below $\alpha \to \infty$. This discrepancy can be explained either in terms of a change in the intrinsic thermal conductivity of the ZnS matrix with the presence of the diamond particles,

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7.CONCLUDING REMARKS

Recent experiments with metal-ceramic interfaces have sought to probe the relationship between the atomic structure and the cohesive strength of interfaces [23]. It is conceivable that a greater mechanical strength of interfaces will be related to its thermal boundary resistance. One approach would be to estimate the frequency of the dominant phonon that carries heat across the interface. The inverse cube dependence of the thermal boundary resistance on temperature means that only a small shift in the effective transition temperature (which is normally the Debye temperature in the acoustic mismatch theory) can produce a very large increase in the thermal boundary resistance in the high temperature regime. Since the dominant phonon frequency is proportional to temperature, even a small change in the effective elastic constant at the interface can produce a significant change in the transition temperature where the thermal boundary resistance changes from T^{-3} behavior to temperature independent behavior. Since the phonon wavelengths near the Debye temperature are of the order of the lattice spacing, even narrow interfaces could have a measurable influence on the scattering of the high frequency phonons near the transition temperature. Perhaps, the time has come to think of boundary thermal resistance in terms of our recent understanding of the structure and mechanical properties of interfaces.

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Figure Captions

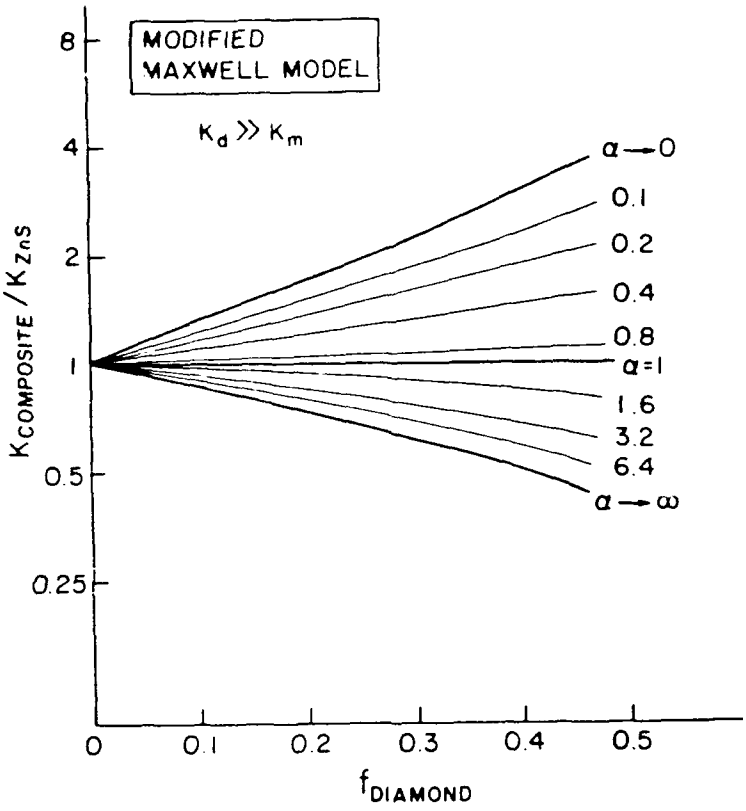
1. Plots of equations (9) and (16) for the modified Maxwell and Bruggeman models showing the effect of the microstructure, in this case the particle size, on the conductivity of the composite. The sensitivity to the microstructure arises because of the high thermal resistance of the interfaces. The parameter $\alpha=a_K/a$ combines the effect of the interface resistance, through the Kapitz radius a_K, and the particle radius on the thermal conductivity of the composite. When $\alpha=1$, the effective conductivity of the particles is the same as that of the matrix because the higher conductivity of the particles is exactly balanced by the higher resistance of the interfaces.

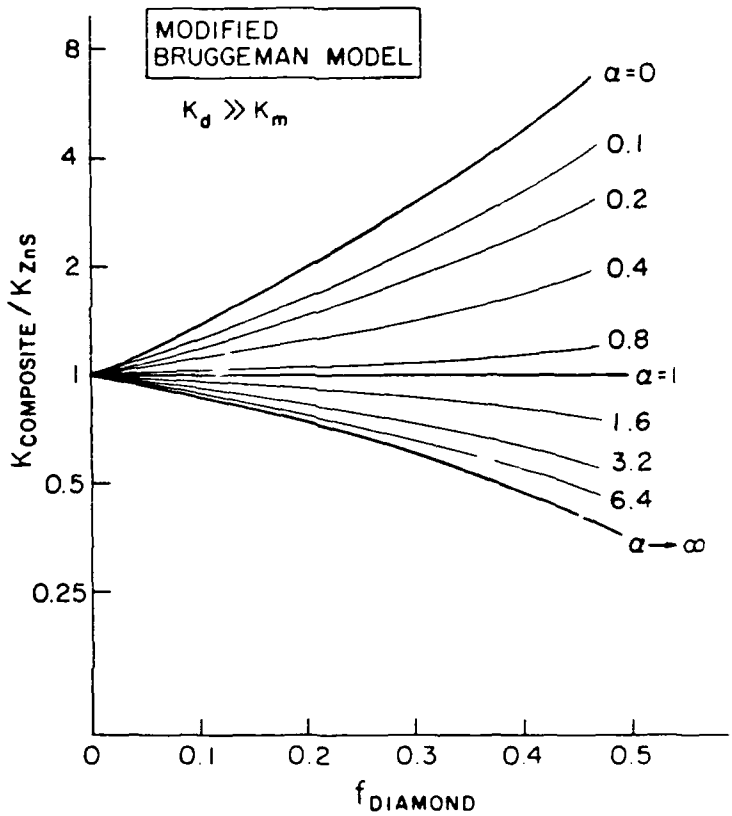
2. Measurements of the thermal diffusivity of the ZnS/D composite as a function of the volume fraction of the diamond, for two different particle sizes of diamond. Note that the small particles lower the thermal conductivity of the composite even though diamond itself is much more conducting than ZnS.

3. A comparison of the data presented in Fig. 2 and the modified Bruggeman model that assumes spherical particle shapes. The small particle data is believed to lie below the $\alpha\rightarrow\infty$ limit because of the nonspherical shape of the diamond particles.

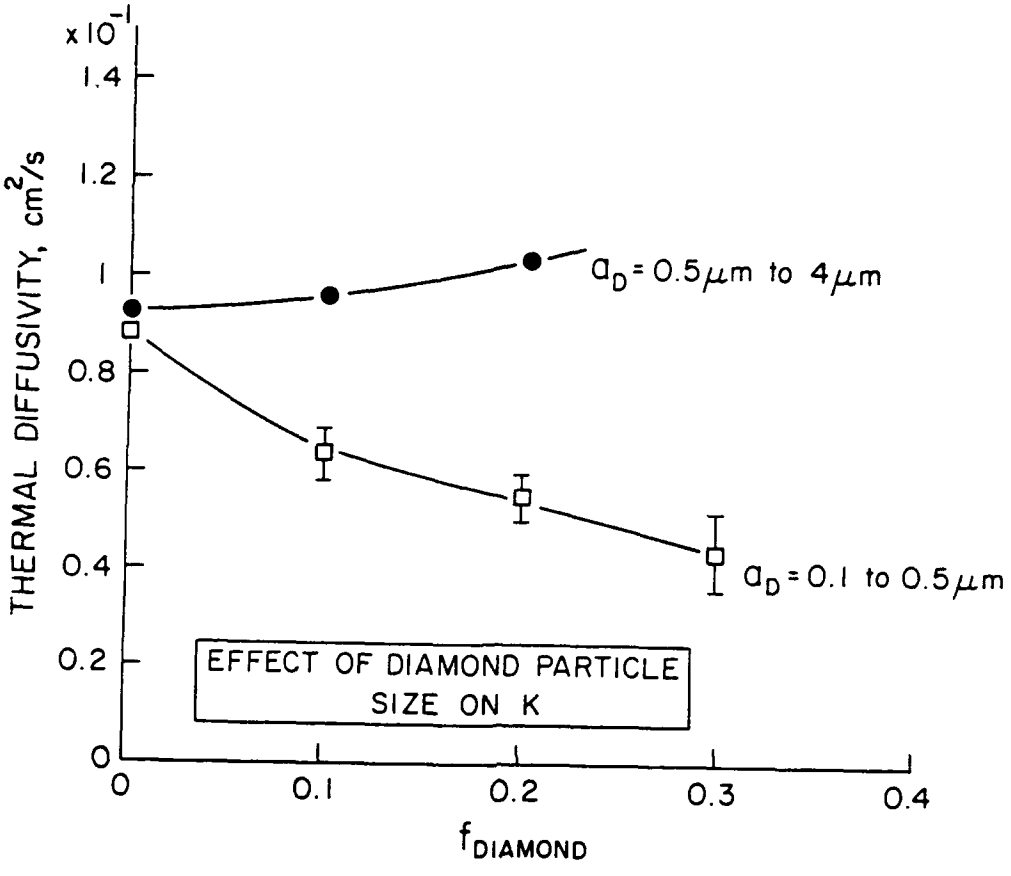
4. A silhoutte of a scanning-electron-micrograph of diamond particles diamond particles embedded in a polycrystalline ZnS matrix. This specimen contained 30 vol % diamond. Although the individual diamond particles themselves are not greatly non-

spherical, the fact that they are distributed in a network configuraton may make them effectively more anisotropic.

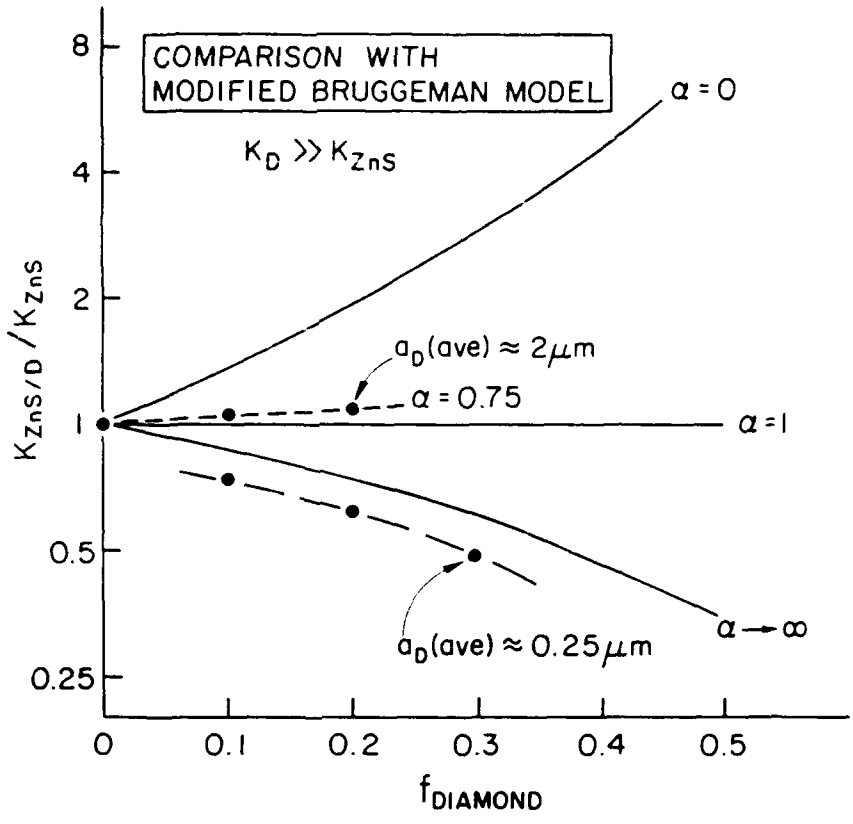




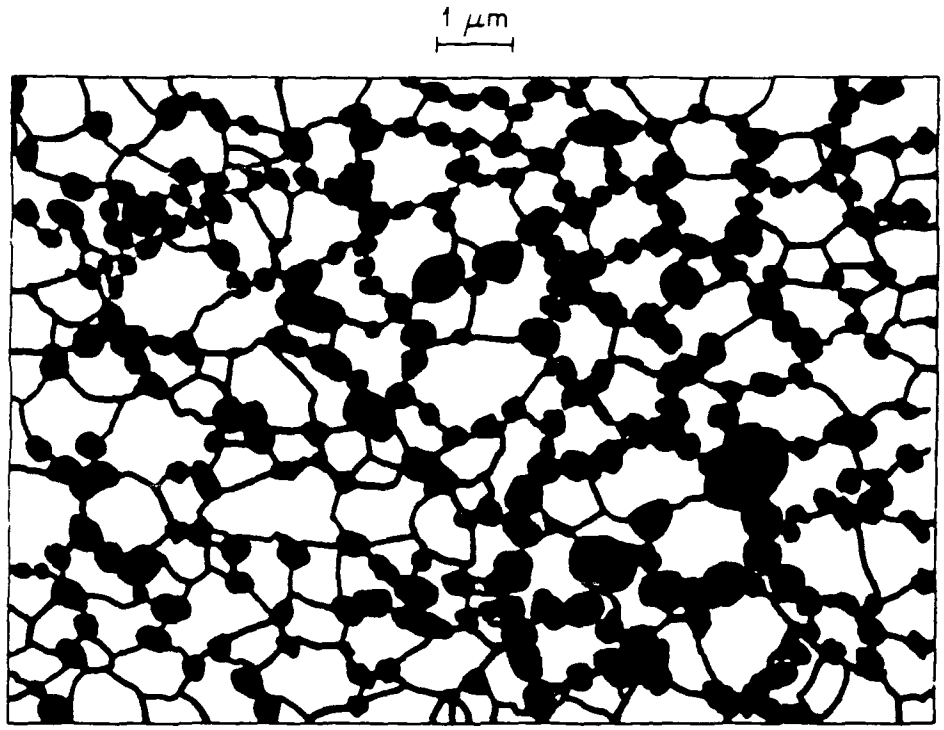
1. Plots of equations (9) and (16) for the modified Maxwell and Bruggeman models showing the effect of the microstructure, in this case the particle size, on the conductivity of the composite. The sensitivity to the microstructure arises because of the high thermal resistance of the interfaces. The parameter $\alpha = a_K/a$ combines the effect of the interface resistance, through the Kapitz radius a_K, and the particle radius on the thermal conductivity of the composite. When $\alpha = 1$, the effective conductivity of the particles is the same as that of the matrix because the higher conductivity of the particles is exactly balanced by the higher resistance of the interfaces.



2. Measurements of the thermal diffusivity of the ZnS/D composite as a function of the volume fraction of the diamond, for two different particle sizes of diamond. Note that the small particles lower the thermal conductivity of the composite even though diamond itself is much more conducting than ZnS.



3. A comparison of the data presented in Fig. 2 and the modified Bruggeman model that assumes spherical particle shapes. The small particle data is believed to lie below the $\alpha \to \infty$ limit because of the nonspherical shape of the diamond particles.



DIAMOND PARTICLES IN POLYCRYSTALLINE ZnS

4. A silhoutte of a scanning-electron-micrograph of diamond particles diamond particles embedded in a polycrystalline ZnS matrix. This specimen contained 30 vol % diamond. Although the individual diamond particles themselves are not greatly non-spherical, the fact that they are distributed in a network configuraton may make them effectively more anisotropic.