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Effect of neutron irradiation on the low-temperature specific heat and thermal conductivity of magnesium oxide

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The specific heat and thermal conductivity of neutron-irradiated MgO have been measured to 0.1 K. There is no evidence for the existence of the localized excitations found in glassy materials or found in neutron-irradiated crystalline SiO_2. This result is consistent with the suggestion that polymorphism is conducive to the formation of an amorphous phase and to the existence of the localized excitations.

INTRODUCTION

At low temperatures, the thermal, elastic, and transport properties of amorphous materials differ greatly from those observed in crystalline solids. In addition, this behavior is similar for nearly all glassy materials independent of the chemical composition.[1] The low-temperature behavior may be ascribed to localized excitations, each having a ground state and one excited state of energy E well separated from other states of higher energy. The energy distribution $n(E)$ is broad and nearly independent of E. It has been proposed that these excitations arise from some entity which tunnels quantum mechanically between two potential-energy minima.[2,3] The low-energy localized excitations also occur with roughly the same spatial density in various crystalline materials.[4] As one example, the presence of the excitations in neutron-irradiated crystalline quartz has been persuasively demonstrated through measurements of ultrasonic attenuation,[5] phonon echos,[6] specific heat,[7] and thermal conductivity.[7] The purpose of the present paper is to inquire if neutron irradiation of other crystalline solids will also create the two-level localized excitations found in glasses.

It has been pointed out that the many polymorphs of SiO_2 are conducive to the formation of a glass,[8-10] and it has been suggested[11] that the localized excitations may arise from displacive rearrangements between the several phases. As a consequence of these observations, one might expect that neutron irradiation of MgO would not produce the localized two-level excitations found in glasses, as MgO appears to occur only in the cubic phase known as periclase. In the measurements discussed below, we do indeed observe that neutron irradiation of MgO fails to create a recognizable density of localized excitations.

EXPERIMENTAL DETAILS

Samples of dimensions $\approx 0.3 \times 0.5 \times 2.5$ cm^3 and mass ≈ 1.3 g were cut from adjacent positions of a single crystal of MgO. All surfaces were sandblasted with abrasive powder. One sample was reserved as a reference and two were irradiated in the CP-5 reactor at Argonne National Laboratory for 14 h and 280 h, respectively. The samples will thus be designated as 0 h (unirradiated), 14 h, and 280 h. During irradiation the samples were placed within a sealed aluminum container which was in contact with the cooling water of the reactor. As the mean free path of neutrons in MgO is much larger than the sample thickness, the samples were irradiated uniformly. Table I lists the neutron dose received by each sample in different energy ranges. The γ exposure was $\approx 10^6$ R/h, the β exposure is not known. Prior to irradiation the samples were colorless. Following irradiation, sample 14 h was uniformly purple and sample 280 h was uniformly deep purple. After irradiation, the samples were etched in acid to remove surface contamination.

The mass densities of the samples are also listed in Table I to an accuracy of 0.3%. Within this accuracy, irradiation exposure caused no change in mass density. In addition, x-ray diffraction peaks remained sharp and characteristic of cubic MgO.

The thermal conductivities and heat capacities were measured as described in Ref. 7 for neutron-irradiated crystalline SiO_2. In the present work, the addenda for the heat-capacity measurements were reduced by a factor of 2. The heat capacity of sample 0 h plus addenda is shown in Fig. 1. Subtraction of the heat capacity of the addenda produces the dashed line which is in agreement with the data of Ref. 12 obtained at temperature $T \gtrsim 9$ K. Since neutron irradiation produced small changes in the specific heat C, only the differences in C/T^3 between samples 14 h and 0 h or between samples 280 h and 0 h are plotted in Fig. 2.

The thermal conductivities are shown in Fig. 3 for the three samples. The data have been divided by T^3 to allow a substantial expansion of the vertical scale. The results for the irradiated samples are very like the data reported in Ref.

TABLE I. Neutron-irradiation dose and mass densities of the three MgO samples.

Sample	0 h	14 h	280 h
0–0.5 eV (cm^{-2})	0	3.0×10^{18}	6.0×10^{19}
0.5 eV → 0.1 MeV (cm^{-2})	0	1.1×10^{18}	2.2×10^{19}
0.1 MeV → ∞ (cm^{-2})	0	1.5×10^{18}	3.0×10^{19}
density ($g\,cm^{-3}$)	3.59	3.58	3.58

13 for measurements above 0.4 K on MgO exposed to similar doses of irradiation. The thermal conductivity of unirradiated sample 0 h has a T^3 dependence indicative of phonon scattering by the abraided surfaces, but the magnitude is $\approx\frac{1}{2}$ that expected.[14] Effects of phonon focusing were not included in the calculation of boundary scattering. Figure 4 shows the intrinsic thermal conductivity of sample 280 h after the effects of boundary scattering, as experimentally measured for sample 0 h, have been subtracted.

DISCUSSION

Several features in Figs. 2 and 3 must be discussed to determine if there is evidence for "glassy" behavior. By glassy behavior we mean a contribution to the specific heat linear in T and a thermal conductivity proportional to T^2. For convenience the localized excitations occurring in glassy materials will be designated as TLS excitations to differentiate them from other excitations created by exposure to neutron and γ irradiation.

In Fig. 3, a minimum occurs in the phonon mean free path l of sample 14 h near $T_R = 1.2$ K. A minimum in l at low temperatures is indicative

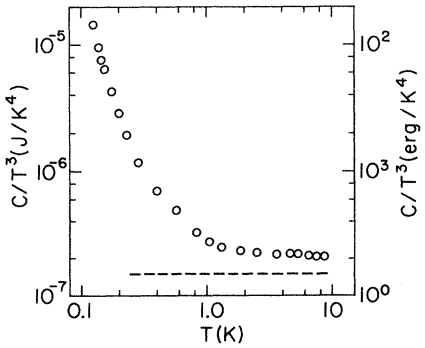

FIG. 1. Heat capacity, divided by T^3, of the 1.34-g unirradiated MgO sample 0 h including addenda. Subtraction of the addenda contribution gives the dashed line.

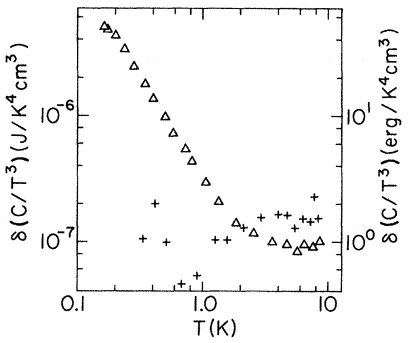

FIG. 2. Difference δ in C/T^3 between MgO samples 14 h and 0 h (symbol Δ), or between samples 280 h and 0 h (symbol +), caused by neutron irradiation. Below 1 K, C/T^3 was large and nearly the same for samples 280 h and 0 h, causing considerable scatter in the difference δ. An earlier measurement of sample 14 h having larger mass gave the same specific heat below 4 K to within 2% and hence these data are not shown.

of a resonant phonon scattering process, and has been reported previously[13] for neutron-irradiated MgO. The width of the peak in thermal resistance $(1/\kappa)$ at half maximum is $\approx kT_R$, which means that the limited frequency resolution inherent to thermal conductivity measurements masks any details concerning the resonant interaction between phonon and defect. Since the number of defects is not sufficient in sample 14 h to produce a Schottky peak in C/T^3 near 1 K in Fig. 2, the strength of the phonon-defect interaction must be large. As noted in Ref. 13, additional neutron irradiation reduces the resonant scattering near 1 K; see κ/T^3 for sample 280 h in Fig. 3. Increased irradiation does intensify a second phonon scattering peak near 20 K which is best seen in the higher-

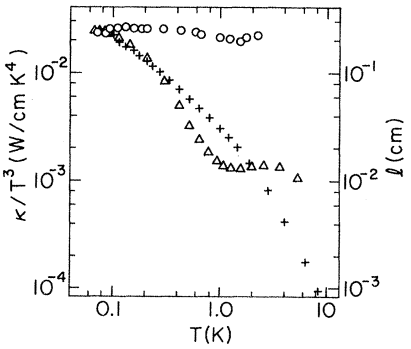

FIG. 3. Thermal conductivity of MgO samples 0 h (○), 14 h (Δ) and 280 h (+) versus temperature. The data are divided by T^3 to permit expansion of the vertical scale and to emphasize departure from a T^3 temperature dependence. The same symbols are used in all figures. The scale on the right provides a rough indication of the phonon mean free path.

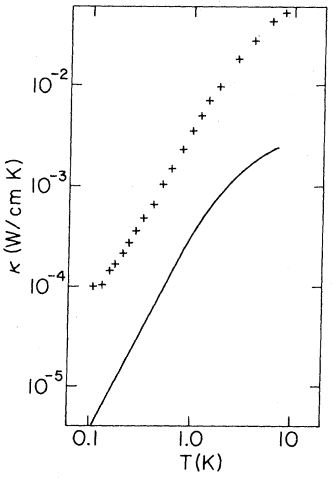

FIG. 4. Thermal conductivity of neutron irradiated MgO sample 280 h after subtracting the phonon scattering measured in the unirradiated sample 0 h. The solid line represents the data for a sample of crystalline SiO_2 neutron irradiated for 270 h in the same reactor, from Ref. 15.

temperature measurements of Ref. 13. The specific-heat data of Fig. 2 for sample 280 h suggest an increased density of excitations near 10 K, but data to higher temperatures are needed to be certain that the increase is related to the minimum in κ/T^3 near 20 K.

The specific heat of sample 14 h has been increased by neutron irradiation, especially at temperatures below 1 K. The temperature dependence and the magnitude of this increase is similar to that observed in crystalline SiO_2 at a similar low exposure to neutron irradiation.[7] In SiO_2 the additional specific heat is removed by continued irradiation, as for the MgO (Fig. 2). Also in SiO_2 the excitations responsible for the increased specific heat do not scatter phonons strongly. Indeed, for MgO in Fig. 3, there is no evidence for an additional phonon scattering mechanism at $T \lesssim 0.4$ K for sample 14 h. After subtraction of boundary scattering, the mean free path in sample 14 h continues to increase rapidly with decreasing temperature.

Thus for MgO sample 14 h we find no evidence for two-level state (TLS) excitations, though at least three other excitations have been created by the neutron or γ irradiation. Indeed, if TLS excitations were to occur, they should be more prevalent in the more irradiated sample 280 h.

The specific heat of sample 280 h has not been significantly increased by neutron irradiation. At 1 K or below any increase in C/T^3 is $\lesssim 10^{-7}$ J/K^4 cm^3 ($\lesssim 1$ erg/K^4 cm^3). For a single crystal of SiO_2 irradiated in the same reactor for 270 h, the TLS excitations contribute $C/T^3 \approx 3 \times 10^{-5}$ J/K^4 cm^3 near 0.2 K.[7] Hence a similar exposure produces a factor of ≥ 300 *fewer* TLS excitations in MgO.

The intrinsic thermal conductivity of the MgO sample 280 h is shown in Fig. 4. Recall that the phonon scattering for this figure is caused only by defects induced by neutron irradiation. The temperature dependence is similar to that found[7] for crystalline SiO_2 (the solid line in Fig. 4) irradiated for 270 h. If we assume that the scattering in the 280-h MgO sample is also caused by TLS excitations, then an estimate may be obtained for the magnitude of the coupling constant γ between phonons and the TLS excitations.[15] For the MgO sample, γ is larger than in SiO_2 by a factor of roughly $\geq \sqrt{300/14} = 4.6$. The factor of 300 is from the ratio of specific heats near 0.2 K, while the factor of 14 is for the ratio of thermal conductivities near 0.2 K. Since γ for SiO_2 is ≈ 1 eV, γ for MgO would be ≥ 4.6 eV. This is a much larger value than observed thus far for any amorphous solid or disordered crystal, and suggests that the thermal conductivity of MgO sample 280 h is not limited by phonon scattering from TLS excitations.

In summary, we find in MgO exposed to neutron irradiation a density of localized excitations a factor of ≥ 300 smaller than that produced in crystalline SiO_2 by the same radiation dose.[16] This result is consistent with the suggestion that polymorphism is conducive both to the creation of amorphous solids and to the existence of the localized excitations found in amorphous materials.

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