

## SEARCH FOR SURFACE MODES OF LATTICE VIBRATIONS IN MAGNESIUM OXIDE\*

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There has been considerable theoretical interest in the effect of boundaries on lattice vibrations of monatomic and diatomic crystals.<sup>1-4</sup> Free boundaries cause two distinct types of surface modes in diatomic crystals, which are in some respects similar to the localized modes of crystals containing defects. The first type has acoustical character and is analogous to the Rayleigh waves in continua. The second type is derived from the optical branch and has no analog in continua.

In comparison with the theoretical efforts, only little experimental work has been performed on this subject. Comparative measurements of the Debye-Waller factor<sup>5,6</sup> and the specific heat<sup>7,8</sup> of bulk samples and microcrystals of a few metals and simple compounds were the only experiments which could be found in the literature. To the authors' knowledge no attempts have ever been made either to gain information about the dependence of the frequency spectra on the grain size of the substances by inelastic neutron scattering or to detect optical surface modes by infrared techniques.

In the following, inelastic neutron-scattering experiments will be reported which were performed on crystalline samples of magnesium oxide with various grain sizes in order to get information about the change of the frequency spectrum due to surface effects. From experimental as well as theoretical points of view,

magnesium oxide was chosen as a sample material. It exhibits mainly heteropolar character of binding, a high Debye temperature, and a high neutron-scattering cross section. Furthermore, there exist convenient techniques to produce microcrystals in several ways.

In the experiments described below, a set of four different MgO samples was used whose properties are summarized in Table I. The samples were examined by electron-microscope as well as x-ray methods. The inelastic neutron-scattering spectra were taken on a conventional rotating-crystal spectrometer<sup>9,10</sup> at an angle of 100° with a primary neutron energy of 22.2 meV. The samples were heated during the scattering experiments up to a temperature of 800°K in order to make negligible the contribution of adsorbed gases and water vapor. The thicknesses of the samples were chosen in such a way that the transmissions were kept between 88 and 94%, so that multiple scattering did not have to be considered.

The phonon frequency distributions were derived from the scattering data by means of the incoherent approximation using the formulas given by Sjölander<sup>11</sup> and Marshall and Stuart.<sup>12</sup> In the computations, second-order down-scattering overlap, multiphonon events, detector efficiency, and instrumental resolution were taken into account.

The applicability of the incoherent approx-

Table I. Sample properties.

Sample designation	Preparation technique	Mean size and shape of the particles	Fraction of surface atoms (%)	Specific surface (m <sup>2</sup> /g)
MgO-10%	MgCO <sub>3</sub> heated 60 min at 650°C	110 Å Irregular	10	150
MgO-5%	MgCO <sub>3</sub> heated 75 min at 750°C	230 Å Irregular	5	70
MgO-1%	MgO smoke	1250 Å Regular cubes	1	13
MgO-0%	Single-crystal fragments	50 μ Irregular	≈0	0.03

imation for our diatomic, mainly coherent scatterer is supported for our experimental conditions by the following facts: (a) Computations of the coherence terms on the basis of a Debye model give only small deviations from the incoherent weight factor. (b) The frequency spectra derived from measurements at the scattering angles of  $80^\circ$  and  $90^\circ$  are in accordance with the spectrum derived from the scattering data at the angle of  $100^\circ$ . (c) The frequency distribution of the sample MgO-0% is in good agreement with that computed by Peckham.<sup>13</sup>

Figure 1 shows the phonon-frequency distributions for the samples MgO-0%, MgO-5%, and MgO-10%, all normalized to unity. In Fig. 2 the more conclusive difference spectra between the frequency distributions of the fine powder samples and that of the bulk sample MgO-0% are given. The difference spectra exhibit four regions I, II, III, and IV, in which the microcrystals show a higher number of modes than the macrocrystals.

The increase of the number of low-energy modes in the samples MgO-5% and MgO-10% may exhibit the existence of acoustical surface

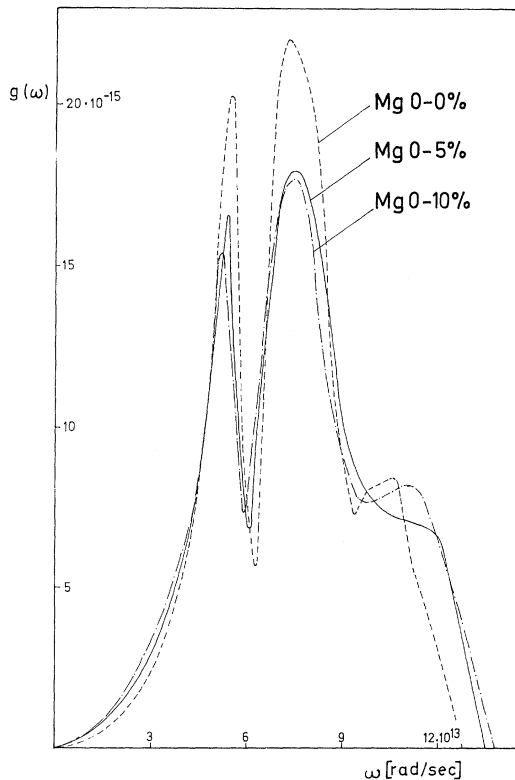


FIG. 1. Phonon-frequency distributions for the samples MgO-0%, MgO-5% and MgO-10%.

modes. It is this increase which is responsible for the increase of the low-temperature specific heat as well as for the decrease of the Debye-Waller factor found in many cases for fine powders.<sup>5-8</sup> The sharp peak II at  $\omega = 6.3 \times 10^{13}$  rad/sec may be explained by the existence of the optical surface modes predicted in the various theoretical publications mentioned above. The strong increase IV, as well as the increase of the cutoff frequency found for the samples MgO-5% and MgO-10%, indicates the existence of a further band of modes specific for microcrystals. It can be seen from Fig. 2 that the number of modes in the regions I, II, and IV increases with decreasing crystal size. This dependence proves that the change of the number of surface atoms is responsible for these changes of the frequency spectrum. By the same reasoning, the peak III does not seem to be caused by surface modes, since the number of modes in this region is higher for the sample MgO-5% than for the sample MgO-10%. Whether the vibrations in the bands

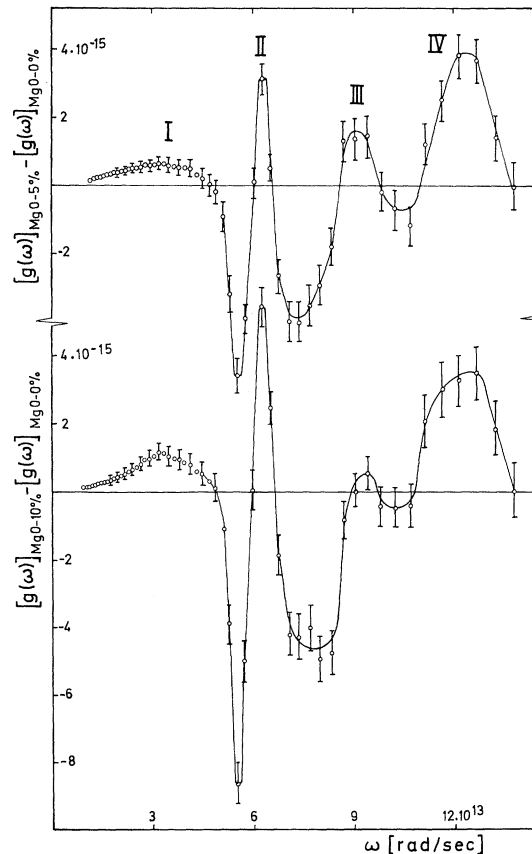


FIG. 2. The distributions  $[g(\omega)]_{\text{MgO-5\%}} - [g(\omega)]_{\text{MgO-0\%}}$  and  $[g(\omega)]_{\text{MgO-10\%}} - [g(\omega)]_{\text{MgO-0\%}}$ .

II, III, and IV are optical in character or not can be decided at present only by infrared experiments.

Marshall and Wilenzick<sup>14</sup> have discussed a low-frequency cutoff in the lattice spectra of microcrystals. In MgO-10% this cutoff should occur at approximately  $5 \times 10^{12}$  rad/sec if the surface atoms are completely free to move. Unfortunately, the limited instrumental resolution does not permit the direct observation of such a low cutoff frequency. But it was found that the low-energy part of the frequency spectra of MgO-5% and MgO-10% shows a  $\omega^{1.9}$  dependence instead of the  $\omega^2$  dependence which is required by theory and was indeed obtained with the sample MgO-0%. This departure may be caused by the low-frequency cutoff.

The results obtained with the samples MgO-5% and MgO-10% could in general be confirmed by measurements using the sample MgO-1%, which consisted of practically fault-free microcrystals. Unfortunately, the statistical error in the difference spectrum was too large to observe the peak III, so that only a slight increase of the number of modes in the regions I and IV could be registered.

With the aid of the frequency spectra derived from our experiments, the Debye temperatures of the various MgO samples were computed by equating the exact Debye-Waller exponent with the one derived from the Debye model.<sup>10</sup> The values of the resulting Debye temperatures are

$$770 \pm 8^\circ\text{K for MgO-0\%,}$$

$$735 \pm 10^\circ\text{K for MgO-5\% (4.5\% decrease),}$$

$$720 \pm 10^\circ\text{K for MgO-10\% (6.5\% decrease).}$$

Barron *et al.*<sup>7</sup> have derived from specific-heat measurements on bulk samples of magnesium oxide a Debye temperature of 770°K for sample temperatures beyond 300°K. The same authors derived from the specific-heat data of Giauque and Archibald<sup>8</sup> a Debye temperature

of 740°K for magnesium oxide microcrystals with a mean grain size of 250 Å. Both results are in very good agreement with the values computed from the measured frequency spectra of the samples MgO-0% and MgO-5%.

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