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Raman Scattering from Microcrystals of MgO

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We have observed the Raman scattering spectrum from finite crystals of MgO. Lines have been observed at 595, 719, and 1096 cm^{-1}. Very good agreement is obtained between the observed lines and the lattice dynamic theory of finite crystals. However, no agreement is obtained with the macroscopic theory.

The nature of vibrations of finite crystals has received a great deal of both theoretical and experimental interest recently. In this Letter we wish to report what we believe to be the first direct observation of such vibrations by Raman spectroscopy. We have observed the modes of vibration in cubic microcrystals of MgO.

Theoretical investigations of such modes have followed two directions: (1) a macroscopic approach, and (2) a lattice dynamic approach. Although most of the theoretical work has been carried out on a slab geometry, we will only consider work done on a spherical geometry as this geometry is more representative of our experimental conditions. Fröhlich[1] first investigated the modes of vibration of an isolated sphere using the macroscopic approach. He assumed the radius of the sphere to be small with respect to the wavelength of the polarization wave. For an ionic crystal of cubic symmetry only one vibrational mode was found to occur lying between the transverse optic frequency ω_T and the longitudinal optic frequency ω_L of the bulk crystal. Fuchs and Kliewer[2] and Ruppin and Englman[3] have extended Fröhlich's result to other geometries and have refined Fröhlich's calculations for the sphere. Fuchs and Kliewer[2] have solved the wave equation for the sphere, and Ruppin and Englman[3] have included both retardation effects and the effects of a dielectric media surrounding the sphere. Two series of modes then result. One series lies in the gap between ω_T and ω_L and a second series lies below ω_T. Genzel and Martin[4] and more recently Barker[5] have attempted to include the effect of neighboring particles on the effective dielectric function of the macroscopic theory and have included this effect on the vibrational modes.

Maradudin and Weiss[6] have approached the problem of finite crystals from the lattice dynamic viewpoint, and have employed the Kellermann model of cubic ionic crystals.[7] They have found two vibrational modes for cubic crystals which lie between ω_T and ω_L. These modes become degenerate for spherical crystals when $k=0$, where $\vec{k}$ is the wave vector of the mode. As k increases, one mode tends towards ω_L and the other tends towards ω_T. Lucas[8] has modified the results of Maradudin and Weiss for spherical particles to include retardation effects with the result that the degeneracy at $k=0$ is lifted. One mode is the same as obtained by Maradudin and Weiss and lies in the gap between ω_T and ω_L for k large. The other mode has frequency greater than ω_L and tends to the line $\omega=kc$. The dispersion curves are given by Lucas. It is seen that the macroscopic theory and the lattice dynamic theory give very different results for the vibrational modes of a sphere.

Experimental results on the modes of finite crystals of MgO have been reported by several

authors. Neutron scattering,[9] electron scattering,[10] and infrared absorption[4,11-14] have been used. However, in many cases the nature of the surface and the particle size have not been well defined, and the resolution is generally poor. The results of these experiments are not consistent and in large part do not correlate well with the present theories.

We have selected MgO for our Raman scattering experiments for several reasons: (1) MgO is a cubic crystal and therefore in the bulk has no first-order Raman spectrum as it possesses inversion symmetry; (2) a large gap exists between ω_L and ω_T of 330 cm^{-1}; (3) it is an ionic crystal of excellent physical stability that can be produced in powders of microcrystals of high purity and uniform size ranging from 100 Å to over 1000 Å; and (4) the physical constants of MgO are well known. We have grown microcrystals of MgO by three techniques: burning magnesium ribbon in air, thermal decomposition of $Mg(OH)_2$, and thermal decomposition of $MgCO_3$. Experiments were also performed on a commercial MgO powder. The particle size was measured by electron microscopy and by x-ray line-broadening methods. The single-crystal nature of the crystals was established by electron diffraction. The crystal purity was determined to be better than one part in 10 000. The experiments were performed using an argon-ion laser as a source, and the usual photon-counting detection technique. Two spectra taken at room temperature are reproduced in Fig. 1 for MgO particles of 300 and 600 Å average particle size. The two spectra were taken under identical experimental conditions. It has been observed that the lines are not strongly temperature dependent and do not depend on the environment of the crystals. Three lines are observed at 595, 719, and 1096 cm^{-1} for 300 Å particle size. As can be seen, the strength of the observed lines is strongly dependent on crystal size, the broad line at 719 cm^{-1} being barely visible for the larger particle size.

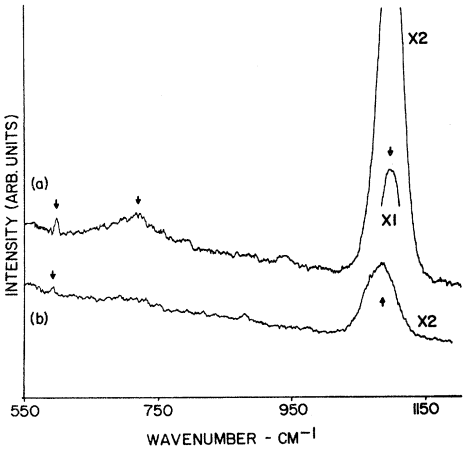

FIG. 1. Chart recording of the Raman spectra of microcrystals of MgO at room temperature produced by thermal decomposition of $MgCO_3$. Curve *a* is for 300 Å average particle size and curve *b* is for 600 Å average particle size.

Unlike the macroscopic theory, the lattice theory of Lucas[8] does predict a mode above the longitudinal optic mode of the bulk. For $k=0$ Lucas predicts two modes, given by

$$\omega_+^2 = (e^2/\mu r_0)(6r_0^4/\kappa e^2 + 2\pi), \quad (1)$$

$$\omega_-^2 = 6r_0/\mu\kappa, \quad (2)$$

where e is the effective charge, μ is the reduced mass of the cation and anion, r_0 is the lattice constant, and κ is the bulk compressibility. Substituting the known physical constants for MgO we obtain for the two modes at $k=0$ the values of 609 and 1105 cm^{-1}. As k increases, the line at 609 cm^{-1} becomes asymtotic to the value of the longitudinal optic mode of the bulk crystal which is at 730 cm^{-1}. The theoretical dispersion curve for these two modes for particles of 600 Å radius is shown in Fig. 2. The Kellermann model[7] does not give the correct values for the bulk optic frequencies of MgO, and therefore the limiting frequency in Fig. 2 is too high. The observed frequencies are in close agreement with the frequencies calculated from the lattice dynamic theory of the modes of finite crystals as calculated by the Kellermann theory for the $k=0$ modes and from the limiting frequency of the low-frequency mode, i.e., ω_L. It should be pointed out that according to the lattice dynamic theory these three frequencies should be size independent. In our experiment we observe a slight shift to lower frequency with increasing particle size, a shift from 595 to 592 cm^{-1} for the low-frequency mode and a shift from 1096 to 1088 cm^{-1} for the high-frequency mode as the particle size is increased from 300 to 600 Å. Also according to the Lucas theory the dispersion curves have zero slope at these three frequencies so the density of states is high there. Raman scattering is known to be strong at these so-called critical points. Also, we need not consider wave-vector conservation for particles of the size considered as the uncertainty in the wave vector of the mode would be of the order of R^{-1}, where R is the radius of

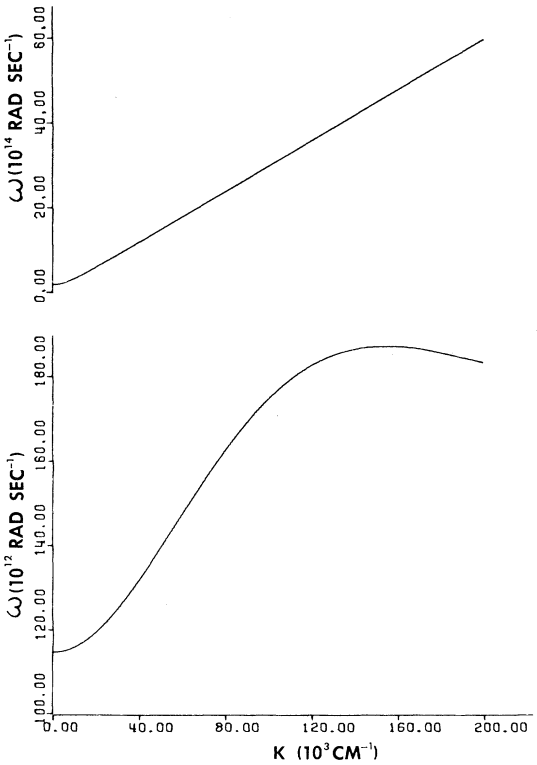

FIG. 2. Calculated dispersion curves for the two high-frequency modes of 600-Å particles of MgO. The curves were calculated using the theory of Lucas (see Ref. 8).

the particle.

Therefore, our experimental results correlate very well with the lattice dynamic theory of the modes of a sphere. We believe the technique of Raman scattering to be a very useful method of studying the nature of the vibrations of finite solids and are currently working to elucidate further the nature of these modes in microcrystals of MgO and other crystal types.

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