PHYSICAL REVIEW B VOLUME 18, NUMBER 2 15 JULY 1978

Infrared absorption in MgO microcrystals

T. S. Chen, F. W. de Wette, and Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712

(Received 10 March 1978)

The dependence of the infrared-absorption properties on size variation and surface relaxation of rectangular MgO microcrystals (clusters) has been studied in the context of the rigid-ion model. The frequency ω_m of maximum absorption (for a given polarization direction) increases slightly with increase in cluster size from 180 to 900 ions, and also when surface relaxation of the cluster is taken into account. In all cases studied, ω_m is extremely close to the Fröhlich frequency ω_F for spherical particles treated in continuum theory. The total absorption is independent of crystal orientation and relaxation, and proportional to the number of particles in the cluster.

I. INTRODUCTION

In recent years a fair amount of experimental and theoretical interest has been devoted to the infrared-absorption properties of finite ionic crystals. The problem was first considered by Frölich[1] in 1949, who showed that a spherical specimen of ionic crystal material, with a radius small compared to the wavelength, exhibits an infrared resonance frequency ω_F intermediate between the longitudinal- and transverse-optical frequencies ω_L and ω_T of the bulk material. The first detailed treatments of the infrared-absorption properties of small crystallites were given by Englman and Ruppin[2] and Fuchs and Kliewer[3] in the context of continuum theory and by Genzel and Martin[4] and Martin[5] using lattice dynamics. In addition, a variety of experimental[6-8] and theoretical[9-13] studies of specific materials have been published.

The present work is a sequel to an earlier study[14] of the effects of size variation and surface relaxation on the vibrational properties and the specific heat of rectangular microcrystals of MgO. The dynamical information of this earlier work has been used to calculate the infrared-absorption coefficients of these microcrystals and to examine the effects of size variation and relaxation on their optical-absorption spectrum. This is of particular importance since the earlier (and first) lattice-dynamical work on rectangular microcrystals[4,5] had not addressed the question of surface relaxation and had been carried out for rather small crystallites. The main conclusions of the present work are that the largest contribution to the total infrared-absorption coefficient results from an optical vibration with frequency ω_m, which is extremely close to the Fröhlich frequency ω_F of continuum theory, and which changes only slightly with size variation and relaxation. The experimentally observed downward shift of the infrared-absorption maximum with increasing particle size[8] is the result of the increase in the number of vibrations with frequencies below ω_m which contribute to the absorption; the total absorption is strictly proportional to the particle number and independent of relaxation.

II. CALCULATION AND RESULTS

The lattice-dynamical calculations were performed on rectangular microcrystallites (clusters) of MgO containing $6\times6\times5=180$ atoms and $10\times10\times9=900$ atoms, called the small and the large cluster; the Kellerman rigid-ion model was used to describe the ionic interactions. For details of the calculation we refer to Ref. 14. Here we just mention that these clusters have D_{2h} symmetry (with [001], [110] and $[1\bar{1}0]$ as twofold rotation axes) allowing a significant reduction of the dynamical matrix and leading to a maximum number of independent vibrational frequencies for the cluster.

The infrared-absorption coefficients are calculated for three different cases, namely, for small unrelaxed (S^U) and relaxed (S^R) clusters and for a large relaxed cluster (L^R). In the unrelaxed cluster, the ionic positions are the same as those in the bulk crystal, whereas in the relaxed clusters the ions near the surface moved slightly inward to attain their equilibrium positions. The relaxation procedure is described in Ref. 14.

The mechanism of infrared absorption by the cluster is quite simple. Because the cluster dimensions are small compared to the wavelength of the incident radiation, the cluster is polarized by a time-dependent electric field which is uniform over the cluster, causing the creation of optical lattice vibrations which give rise to the absorption. In the rigid-ion model used here, the cluster polarization is totally the result of the displacements of the point ions. Accordingly, the absorption coefficients $\alpha_\gamma(\omega)$, giving the absorbed intensity of light with frequency ω and polarized in the γ (x,y,z) direction can be expressed in terms of the vibrational eigenfrequencies ω_p and eigenvectors $\xi_p(l\kappa\gamma)$ of the cluster,[4]

$$\alpha_\gamma(\omega) = \sum_{\substack{l\kappa \\ l'\kappa'}} e_\kappa e_{\kappa'} (M_\kappa M_{\kappa'})^{-1/2} \times \sum_p \xi_p(l\kappa\gamma)\xi_p(l'\kappa'\gamma)\delta(\omega_p, \omega) . \tag{1}$$

Here p labels the modes, l and l' are the site indexes, and κ and κ' indicate the type of ion; ϵ_κ and M_κ are the effective charge and the mass of the ion of type κ.

Extensive use of the cluster symmetry (space group D_{2h}) enables us to simplify the calculation of $\alpha_\gamma(\omega)$ substantially, if the coordinate directions x, y, and z are chosen as in Fig. 1. Of the eight one-dimensional irreducible representations of D_{2h} only one gives nonzero contributions to α_γ for any particular polarization direction x, y, or z. For example, for the large crystal there are 2700 normal-mode eigenvectors each consisting of 2700 coefficients for the x, y, and z displacements of the 900 atoms. The three irreducible representations transforming like x, y, and z each contain only 350 normal modes. Thus for any one polarization we need consider only 350 normal modes, Eq. (1) giving zero for the remaining 2350. Symmetry yields a further simplification since for each eigenvector we need consider only the coefficients of the displacement components in the direction of polarization on only atoms in $\frac{1}{8}$ of the rectangular crystallite. This gives 150 coefficients to be considered for the 900-atom crystallite. (This is greater than $\frac{1}{8}\times 900$ because the atoms on the reflection plane surfaces of the $\frac{1}{8}$ crystallite are shared with adjacent $\frac{1}{8}$ crystallites.)

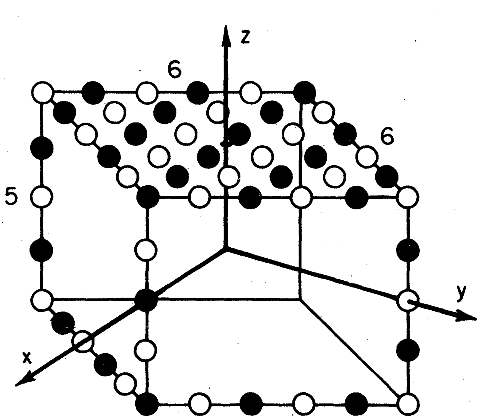

FIG. 1. Small cluster of MgO (180 ions) with D_{2h} symmetry. The choice of the coordinate directions x, y, z is indicated.

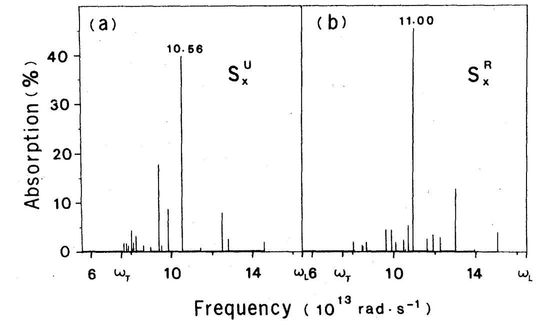

FIG. 2. $\alpha_x(\omega)/\alpha_{\text{total}}$ (in %) for the small unrelaxed (S_x^U) and relaxed (S_x^R) clusters.

As we will see below, the results for $\alpha_\gamma(\omega)$ are dependent on the orientation of the incident electric field with respect to the crystal axes and on cluster size and relaxation. However, it follows directly from Eq. (1) that the total absorption $\alpha_{\gamma,\,\text{tot}} = \sum_\omega \alpha_\gamma(\omega)$ is independent of crystal orientation and relaxation; using the closure property of the eigenvectors, one finds immediately

$$\alpha_{\gamma,\,\text{tot}} = \tfrac{1}{2}\, e_\kappa e_{\kappa'} N (1/M_\kappa + 1/M_{\kappa'}) , \tag{2}$$

where N is the total number of ions in the cluster.

The results of the calculations are given in Figs. 2–4. In Fig. 2 we present $\alpha_x(\omega)$ for the small unrelaxed cluster (S_x^U) and the small relaxed cluster (S_x^R). The α scale is given in percentage of the total absorption $\alpha_{x,\,\text{tot}}$. We notice that many frequencies contribute to $\alpha_{x,\,\text{tot}}$; in fact for most of the contributing frequencies $\alpha_x(\omega)$ is too small to show up in the figure if we use a linear scale for $\alpha_x(\omega)$. We further note that the

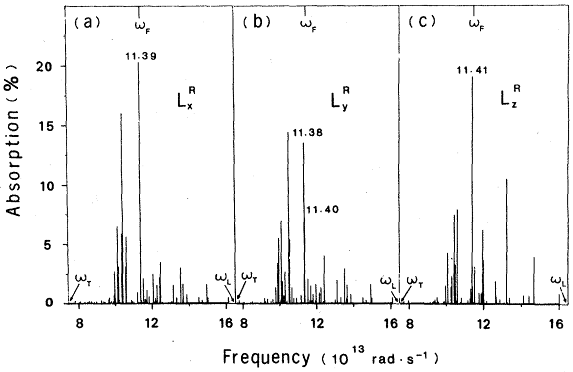

FIG. 3. $\alpha_\gamma(\omega)/\alpha_{\text{total}}$ (in %) for $\gamma = x$, y, and z for the large relaxed cluster.

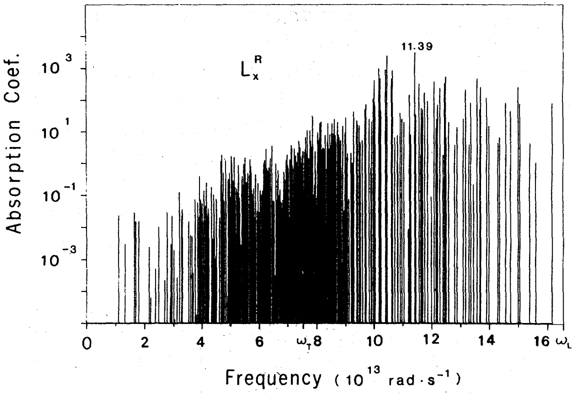

FIG. 4. Logarithmic plot of $\alpha_x(\omega)$ for the large relaxed cluster.

maximum contribution to α_x (more than 40%) occurs at $\omega_m = 10.56 \times 10^{13}$ rad/sec for S_x^U and at $\omega_m = 11.00 \times 10^{13}$ rad/sec for S_x^R.

The occurrence of a frequency of maximum absorption ω_m in the infrared-absorption spectrum of finite crystals is a characteristic and well-known feature. The value of ω_m provides us with a simple way to judge the effects of size variation and of relaxation on the infrared-absorption spectrum of the clusters. In order to pursue this point we present in Table I the values of ω_m for the unrelaxed small cluster (S_x^U, S_y^U, S_z^U), the relaxed small cluster (S_x^R, S_y^R, S_z^R), and the relaxed large cluster (L_x^R, L_y^R, L_z^R); of these only S_x^U, S_x^R and L_x^R, L_y^R, and L_z^R are shown in the figures (Figs. 2 and 3, respectively).

Commenting on these results we first note that relaxation of the small cluster in each of the cases increases ω_m by 3.5% to 4.0% (compare S_x^U to S_x^R, S_y^U to S_y^R, and S_z^U to S_z^R); this is due to a slight stiffening of the forces caused by the inward relaxation of the surface ions. The size variation from 180 and 900 ions increases ω_m by another 3.5% (compare S_x^R to L_x^R, etc.); this again results from a stiffening of the forces but is now caused by the increase in size of the crystallite.

At this point it is interesting to make a comparison with the results of the continuum-theory treatment of the infrared absorption of small spheres of dielectric material. If the radius of the spheres is small compared to the wave length of the incident radiation, Fröhlich's theory[1] indicates that a strong fundamental absorption will occur at the Fröhlich frequency ω_F given by

$$\omega_F^2 = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)]\omega_T^2\,, \tag{3}$$

where ϵ_0 and ϵ_∞ are the static and the high-frequency dielectric constants, respectively. Using the Lyddane-Sachs-Teller relation $(\omega_L/\omega_T)^2 = \epsilon_0/\epsilon_\infty$ and the fact that $\epsilon_\infty = 1$ in the rigid-ion model, we find from Eq. (3)

$$\omega_F^2 = \tfrac{1}{3}\,\omega_L^2 + \tfrac{2}{3}\,\omega_T^2\,. \tag{4}$$

According to the bulk rigid-ion model for MgO used here, we have $\omega_L = 16.74 \times 10^{13}$ rad/sec and $\omega_T = 7.517 \times 10^{13}$ rad/sec; Eq. (3) then gives $\omega_F = 11.45 \times 10^{13}$ rad/sec. This result for ω_F is surprisingly close to the values of ω_m for the rectangular clusters considered here. That such an agreement should exist is plausible from the fact that for a cubical crystallite of homogeneously polarized material, the depolarizing field at the center is the same as for a sphere. However, the closeness of the agreement is unexpected and indicates that continuum theory gives accurate results already for very small particles. Finally we note that relaxation and increase in size not only have non-negligible effects on the ω_m's, but also bring their values into closer agreement with ω_F.

In Fig. 3 we show the results for $\alpha_x(\omega)$, $\alpha_y(\omega)$, and $\alpha_z(\omega)$ for the relaxed large cluster. Note that α_y contains two contributions at the almost degenerate frequencies 11.38×10^{13} and 11.40×10^{13} rad/sec which together about equal $\alpha_x(\omega_m)$ or $\alpha_z(\omega_m)$. The fact that α_y exhibits two maximum contributions while α_x has only one results from the nonequivalence of the x and y directions (cf. Fig. 1).

To exhibit the large number of contributions to α_y, most of which do not show up in Fig. 3, we replot, in Fig. 4, the results for α_x for the large relaxed cluster (L_x^R) using a logarithmic α scale. As mentioned above, because of symmetry, 350 out of a total of 900 x-polarized vibrations contribute to α_x, and all of the contributions appear in Fig. 4. Note that these contributions span almost the entire frequency range, from well below ω_T up to ω_L. According to continuum theory,[15] vibrational modes for finite crystals of arbitrary shape can only have frequencies between ω_T and ω_L, but for lattice-dynamical studies this is not necessarily true as we have shown in

TABLE I. Main absorption frequencies ω_m in 10^{13} rad/sec.

	S_x^U	S_x^R	L_x^R	S_y^U	S_y^R	L_y^R	S_z^U	S_z^R	L_z^R	ω_F
ω_m	10.56	11.00	11.39	10.60	10.97	11.38 11.40	10.64	11.05	11.41	11.45

extensive calculations on slab-shaped crystals.[16] For instance, for a MgO slab, the optically active Lucas modes have a limiting long-wavelength frequency below the transverse-optical bulk band. For crystals of the size we have studied here, the question whether the absorption is caused by a surface or a bulk mode is somewhat academic, because these microcrystals are too small to make a clear distinction. In his work on RbF microcrystals (containing 64 and 144 ions) Martin[5] did indeed make a distinction between the contributions to α from edge, surface, and volume modes, and he ascribed the main absorption as resulting from surface modes. However, as we have seen, this main contribution to α arises from the Fröhlich mode, which in continuum theory is associated with a uniform polarization of the cluster and should therefore be considered as a bulk mode rather than as a surface mode. To make a distinction between edge, surface, or bulk modes for the much larger clusters considered here, one would have to examine, for a given mode, the contribution of the various parts of the crystal to the overall dipole moment. This is not only a major undertaking, but it can only lead to results which are ambiguous at best, even for the 900-ion cluster.

III. DISCUSSION

In this paper we calculated the infrared absorption of rectangular microcrystals of MgO, containing 180 and 900 ions, using the rigid-ion model. The main contributions to the absorption coefficients α_x, α_y, and α_z arise from optical vibrations with frequencies between ω_T and ω_L, the main contribution (~40% for the small cluster and ~20% for the large cluster) coming from a frequency which is exceedingly close to the Fröhlich frequency ω_F of continuum theory. Increase in size and relaxation of the cluster bring the main absorption frequency to within 0.4% of ω_F.

We compare the present results with Genzel and Martin's[4] experimental results on infrared transmission of 0.1-μm cubes of MgO. According to these measurements the absorption occurs in the range ω_T to ω_L, with the main absorption maximum slightly below ω_F and a secondary peak around ω_T. It appears that the present results are in much better agreement with the measurements than Genzel and Martin's calculation for a 48-ion cluster, which gives a peak roughly halfway between ω_F and ω_T. This discrepancy between calculated and measured results is undoubtedly caused by the small size of the cluster used in the calculation of Ref. 4 because, as we have found in the present work, increasing the size of the cluster brings the location of the main absorption frequency closer to ω_F.

We conclude with some qualitative comparisons with earlier work. Bryksin *et al.*[8] have performed measurements and calculations on NaCl microcrystals. For large crystallites (20–40 μm) these authors find a broad infrared-absorption band spanning the frequency range from well below ω_T up to (and above) ω_L. However, the size of these crystallites is of the order of the infrared wavelength. For decreasing crystallite size, the band narrows and becomes concentrated in the range ω_T–ω_L, and the location of the maximum absorption shifts upwards. Discrepancies between these measurements and calculated results for spherical crystallites were attributed to differences in shape, because the experimental sample consisted of cubelike particles. On the basis of the present results it must be concluded that the upward shift of the main absorption peak with decreasing particle size results solely from the increasing importance of the main absorption contribution at ω_m with decreasing size, not to a noticeable shift in ω_m itself [according to Eq. (4), ω_F is size independent]. In fact, we find a slight *decrease* in ω_m with decreasing size. Furthermore, our results seem to indicate that shape differences are unimportant; after all, the frequency of maximum absorption ω_m, calculated with lattice dynamics for cubelike particle, is exceedingly close to ω_F, calculated with continuum theory for spherical particles. As long as the particle shape of an experimental sample is between spherical and cubic, shape dependence should be negligible. This, of course, would not be true for plate- or needle-shaped particles, but these appear not to be formed in the experimental production of powder samples.

These questions about the influence of size and shape on the infrared absorption of microcrystals have also been raised by Ruppin[10] in his more recent study of ZnS microcrystallites. Within the size variation of the microcrystals studied here, these questions have now been answered. Another question raised by Ruppin concerns the high-frequency cutoff of the absorption spectrum. As can be seen from comparing S_x^R in Fig. 2(a) and L_x^R in Fig. 3(a), the increase in size raises the high-frequency cutoff somewhat, but never above ω_L. These conclusions are valid within the rigid-ion approximation. In recent work on the effects of relaxation on the surface vibrational modes of crystal slabs in the shell model, Chen and de Wette[17] have shown that surface relaxation can give rise to surface modes above the longitudinal-optical bulk bands; thus, conceivably, the high-frequency cutoff could lie above ω_L. In fact, this appears to be the case in the experimental work of Bryksin *et al.*

ACKNOWLEDGMENTS

The authors wish to thank Dr. D.G. Dempsey for his consultation and help with the calculations. This work was supported in part by NSF Grant Nos. DMR 75-18492-A01, DMR 73-02449-A02, and DMR 77-21559, and by the Robert A. Welch Foundation.

---

[1] H. Fröhlich, *Theory of Dielectrics*, 2nd ed. (Clarendon, Oxford, 1958).

[2] R. Englman and R. Ruppin, J. Phys. C 1, 614 (1968); R. Ruppin and R. Englman, *ibid.* 1, 630 (1968).

[3] R. Fuchs and K. L. Kliewer, J. Opt. Soc. Am. 58, 319 (1968).

[4] L. Genzel and T. P. Martin, Phys. Status Solidi B 51, 101 (1972).

[5] T. P. Martin, Phys. Rev. B 7, 3906 (1973).

[6] J. T. Luxon, D. J. Montgomery, and R. Summitt, Phys. Rev. 188, 1345 (1969).

[7] T. P. Martin, Phys. Rev. 177, 1349 (1969); Phys. Rev. B 1, 3480 (1970); Solid State Commun. 9, 623 (1971).

[8] V. V. Bryksin, Y. M. Gerbstein, and D. N. Mirlin, Solid State Commun. 9, 669 (1971).

[9] R. Ruppin, Phys. Rev. B 3, 4422 (1971).

[10] R. Ruppin, Surf. Sci. 34, 20 (1973).

[11] L. Genzel and T. P. Martin, Surf. Sci. 34, 33 (1973).

[12] P. Lagarde and M. A. Nerenberg, Phys. Status Solidi B 64, 567 (1974).

[13] R. Fuchs, Phys. Rev. B 11, 1732 (1975).

[14] T. S. Chen, F. W. de Wette, Leonard Kleinman, and D. G. Dempsey, Phys. Rev. B 17, 844 (1978).

[15] R. Ruppin and R. Englman, Rep. Prog. Phys. 33, 149 (1970).

[16] T. S. Chen, F. W. de Wette, and G. P. Alldredge, Phys. Rev. B 15, 1167 (1977).

[17] T. S. Chen and F. W. de Wette, Surf. Sci. (to be published).