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Aggregation effect on the infrared absorption spectrum of small ionic crystals

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The frequency spectrum of clusters of small ionic particles is calculated when the particle mutual interaction is described by a dipole-dipole interaction Hamiltonian. The crystallites are spheres of known bulk dielectric properties. The actual geometry of the cluster is taken into account. Clusters of increasing size (pair, triplet, quadruplet, etc.) have been solved analytically. As expected, the dipolar broadening of the frequency spectrum of (optically active or inactive) surface modes increases with cluster size and compactness. From the spectrum of few-particle clusters, one obtains the long-wavelength modes of large linear or planar aggregates of such clusters by application of the Bloch-Floquet theorem. Application is made to ir optical absorption of NiO. The present approach is intermediate between the continuum model of a structureless powder on the one hand and microscopic calculations for single microcrystals of prescribed shape on the other hand.

I. INTRODUCTION

Powders of small ionic crystal have a broad infrared absorption spectrum spanning a frequency interval between ω_T and ω_L, the frequencies of the long-wavelength transverse and longitudinal optical modes of the bulk material.[1] This is in contrast with the absorption behavior of pure, large, single crystals which consists of a sharper peak at ω_T.[2]

Several broadening mechanisms have been considered.

(a) First, there must exist several *size effects*. Thus, a small ionic sphere whose radius is much smaller than the wavelength of light absorbs mainly at an intermediate frequency ω_S ($\omega_T < \omega_S < \omega_L$) characteristic of the so-called Fröhlich surface mode of the sphere[3] for which the polarization induced by the external ir radiation remains uniform throughout the whole sphere. The appearance of this new mode is a pure surface effect as it results from the particular value of the depolarization field of a spherical boundary. On the other hand, the mere fact of the reduced size must affect the damping of both bulk and surface modes as the crystal surface scatters the phonons just as it does for plasmons[4] and other visible or uv excitations.

(b) Second, there are *sharp effects* for nonspherical particles. Surface, edge, and corner modes have been investigated.[5] The density of optically active modes for small nonspherical microcrystals differs from the bulk density and this also affects the absorption spectrum.

(c) Third, there are *mixed-material effects*. The dielectric response of a powder in suspension is different from the dielectric response $\epsilon_1(\omega)$ of the powder material and also from that $\epsilon_2(\omega)$ of the surrounding medium. Barker[6] and independently Genzel and Martin[7] have introduced the macroscopic concept of an effective dielectric function $\epsilon_{\text{eff}}(\epsilon_1, \epsilon_2, f)$ depending on a phenomenological parameter f proportional to the fractional composition of the suspension in materials 1 and 2. In the theoretical models,[6,7] the particles are assumed to be spheres uniformly distributed in the substrate and f is simply the fractional volume occupied by the particles. Hence, this theory takes into account the interparticle interactions in an average manner.

In the present paper, we wish to consider model calculations for another possible source of broadening, namely, the effect of *aggregation* or *clumping* of small particles together. The model we propose takes into account some pure size effects such as the particles are assumed to be small spheres but we try to include some of the effects due to the *actual state of aggregation* of the powder particles.

We have calculated the frequency spectrum of different clusters of *identical* ionic spheres. Within the clusters, the particles interact via the dipolar interaction. From the spectrum of a few particle clusters, one can also obtain the long-wavelength modes of large linear and planar aggregates of such clusters by application of the Bloch theorem. Although the clusters we study (pair, triplet, quadruplet, chains, etc.) are likely to be present in the powder, the actual, statistical distribution of particles in a given sample is rarely known and this will unfortunately forbid quantitative comparison with experiment.

However, our calculations show that clumping of particles is an important feature for the response of powders to infrared radiation just as it is in the visible and ultraviolet where the shift and broadening of absorption lines are partly responsible for the adhesion of particles together.

In Sec. II, we introduce the model Hamiltonian describing a single ionic sphere. In Sec. III, the response of an isolated cluster of identical spheres to a long-wavelength electric field is obtained. The cooperative effect of oscillating dipoles is evident in the solution of the eigenvalue problem for the interaction Hamiltonian of aggregates. For illustration, we have explicitly presented the case of a tetrahedron cluster. For simpler clusters, we briefly give the relevant modes and relative absorption strengths. Infinite clusters are considered in Sec. IV. They serve as an analytical test beside nicely leading to interesting limiting values. In Sec. V, we illustrate the calculations of the previous sections by applying our results to the case of a "model NiO powder." The numerical values indicate the importance of the clustering effect. Finally, we discuss the range of the optically active modes we have found.

II. SINGLE-PARTICLE MODEL

All particles in the powder are assumed to be spheres of radius R ($\lesssim 1000$ Å) much smaller than the ir wavelength ($\lambda \simeq 20\ \mu$m) and made of a pure material of bulk dielectric function $\epsilon(\omega)$

$$\epsilon(\omega)=\epsilon_\infty+\frac{\epsilon_0-\epsilon_\infty}{1-\omega^2/\omega_T^2}, \tag{1}$$

where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants and ω_T is the transverse optical frequency. Damping is ignored here to concentrate on the pure aggregation effect. Retardation in the propagation of light across the particle diameter can be entirely neglected so that, in the ir radiation, the particle is embedded in an essentially uniform electric field $\vec{E}(\omega)$. Its response is then given by the induced dipole moment[8]

$$e\vec{q}(\omega)=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2}R^3\vec{E}(\omega). \tag{2}$$

The response function has a pole at the frequency ω_S such that

$$\epsilon(\omega_S)+2=0,\quad \omega_S^2=\omega_T^2\frac{\epsilon_0+2}{\epsilon_\infty+2}, \tag{3}$$

which is the condition defining the Fröhlich surface mode for which the induced polarization is uniform throughout the sphere volume.[3]

If we rewrite Eq. (1) in the form

$$e\vec{q}(\omega)=\frac{f(\omega)R^3}{1-\omega^2/\omega_S^2}\vec{E}(\omega), \tag{4}$$

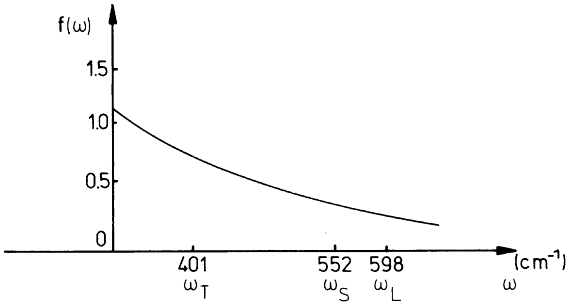


FIG. 1. Function $f(\omega)$, defined by Eq. (7), for the case of NiO: $\epsilon_0=12$, $\epsilon_\infty=5.4$.

one sees that around $\omega \simeq \omega_S$ the sphere responds like a harmonic isotropic oscillator with dynamic polarizability[8]

$$\alpha(\omega)\equiv\frac{f(\omega)R^3}{1-\omega^2/\omega_S^2}=\frac{e^2/m\omega_S^2}{1-\omega^2/\omega_S^2} \tag{5}$$

and the weakly frequency-dependent effective mass

$$m=e^2/f(\omega)R^3\omega_S^2, \tag{6}$$

where

$$f(\omega)=\frac{\epsilon_0-1}{\epsilon_0+2}-\frac{\epsilon_\infty-1}{\epsilon_0+2}\frac{\omega^2}{\omega_T^2}. \tag{7}$$

This function is plotted in Fig. 1 for the case of NiO.

The equation of motion of this (slightly nonlinear) oscillator may be seen to derive from the following isolated sphere Hamiltonian:

$$H=\frac{1}{2}\frac{e^2}{f(\omega)R^3\omega_S^2}\left(\frac{d\vec{q}^2}{dt}+\omega_S^2\vec{q}^2\right)-e\vec{q}\cdot\vec{E}. \tag{8}$$

Indeed, the Hamilton equation of motion $md^2\vec{q}/dt^2 = -\partial H/\partial\vec{q}$ becomes

$$\frac{d^2\vec{q}}{dt^2}(\omega)+\omega_S^2\vec{q}(\omega)=\frac{1}{m}e\vec{E}(\omega), \tag{9}$$

which leads to the correct dynamic polarizability as given by Eq. (5).

In the following, we shall neglect for simplicity higher multipolar orders in the sphere polarization behavior although Hamiltonians for coupled multipolar oscillations may be treated without excessive labor.

III. SMALL AGGREGATE MODELS

We next consider the response to a long-wavelength electric field of an isolated cluster of identical spheres. The spheres are assumed to be in contact with each other and to interact via the dipole-dipole interaction only. Although for contacting spheres, higher-order multipolar coupling occurs, the direct dipolar coupling will clearly be the most important for optical properties.[9]

Our aim is now to obtain the new frequency spectrum of the cluster from the overlap between the electric field of all oscillating spheres. The interaction Hamiltonian of the aggregate has the following form:

$$H = \frac{1}{2}\sum_i \frac{e^2}{f(\omega)R^3\omega_S^2}\left(\frac{d\vec{q}_i^{\,2}}{dt} + \omega_S^2\vec{q}_i^{\,2}\right) + \frac{1}{2}e^2\sum_{i,j}{}' \vec{q}_i \cdot T_{ij} \cdot \vec{q}_j , \tag{10}$$

where $e\vec{q}_i$ is the dipole moment of sphere i and where T_{ij} is the dipolar tensor

$$T_{ij} = -\frac{\partial^2}{\partial \vec{R}_{ij}^2}\,\frac{1}{R_{ij}} = \frac{E_3 - 3\vec{R}_{ij}^0\vec{R}_{ij}^0}{R_{ij}^3} \tag{11}$$

in which $\vec{R}_{ij}$ is the distance between the centers of spheres i and j, $\vec{R}_{ij}^0$ is the corresponding unit vector, and E_3 is the three-dimensional unit matrix.

Since Eq. (10) is quadratic in the $\vec{q}_i$'s, we have an exactly soluble, small oscillations system. The standard solution for the frequencies of oscillations of the normal modes are the square roots of eigenvalues of the dynamical matrix

$$\Omega = \omega_S^2[E_{3N} + f(\omega)T], \tag{12}$$

$$T = \begin{bmatrix} 0 & & & (\mathcal{T}_{ij}) \\ & 0 & & \\ & & \ddots & \\ (\mathcal{T}_{ji}) & & & 0 \end{bmatrix}, \tag{13}$$

$$\mathcal{T}_{ij} = \frac{E_3 - 3\vec{R}_{ij}^0\vec{R}_{ij}^0}{(R_{ij}/R)^3}, \tag{14}$$

where N is the cluster size and E_{3N} is the $3N$-dimensional unit matrix.

If λ_μ designates the $3N$ eigenvalues of T, the eigenfrequencies clearly have the form

$$\omega_\mu = \omega_S[1 + \lambda_\mu f(\omega)]^{1/2}. \tag{15}$$

There is an inconsistency in the notation of Eq. (15) since $f(\omega)$ still represents a frequency-dependent polarizability. In order to solve correctly this nonlinear problem, we may proceed by iteration, introducing the roots ω_μ into $f(\omega)$ and solving again for ω_μ until self-consistency is reached. The λ_μ being purely geometrical factors, depending only on the arrangement of the spheres within the cluster, one has to solve for the roots of

$$\omega_\mu = \omega_S[1 + \lambda_\mu f(\omega_\mu)]^{1/2}, \tag{16}$$

which are

$$\omega_\mu = \omega_S\left(\frac{1 + \lambda_\mu(\epsilon_0 - 1)/(\epsilon_0 + 2)}{1 + \lambda_\mu(\epsilon_\infty - 1)/(\epsilon_\infty + 2)}\right)^{1/2}. \tag{17}$$

For future reference, we note that $\lambda_\mu = 2$ and $\lambda_\mu = -1$ introduced into this formula generate frequencies ω_μ equal to ω_L and ω_T, respectively. Since these are extremal values, one has $-1 \leqslant \lambda_\mu \leqslant 2$ for any cluster.

Neglecting the frequency dependence of the oscillator strength, a good estimate of the optical absorption at frequency ω_μ is given by the square of the total dipole moment of the cluster oscillating in mode (μ). If $\vec{q}_2^{(\mu)}$, $\vec{q}_2^{(\mu)}, \ldots, \vec{q}_N^{(\mu)}$ are the oscillation amplitudes of spheres $1, 2, \ldots, N$, respectively; i.e., the normalized eigenvector of the dynamical matrix Ω for eigenvalue λ_μ, the absorption due to this mode is proportional to

$$A^{(\mu)} = \left|\sum_{i=1}^{N}\vec{q}_i^{(\mu)}\right|^2. \tag{18}$$

Implicit in this result are the assumptions: (i) that the linear dimensions of the cluster are also smaller than the ir wavelength so that all spheres absorb coherently, and (ii) that the cluster may be oriented at random with respect to the ir field so that the average absorption is isotropic. These conditions are largely satisfied in practice. Indeed, with a 20 μm wavelength, the first condition allows for clusters to contain many thousands of particles of 100 Å diameter. The second condition is clearly satisfied with a material in powder form.

We have solved the eigenvalue problem for small-size clusters of various shapes containing two, three, or four spheres, namely, pair, linear triplet, (equilateral) triplet, linear quadruplet, and regular tetrahedron. As an example we discuss here the solution for the tetrahedron illustrated in Fig. 2. Using the coordinate axes and sphere numbering shown in this figure, the T matrix of Eq. (13) is calculated to be the 12-dimensional symmetric matrix

$$T = \begin{bmatrix} 0 & \mathcal{T}_{12} & \mathcal{T}_{13} & \mathcal{T}_{14} \\ \mathcal{T}_{21} & 0 & \mathcal{T}_{23} & \mathcal{T}_{24} \\ \mathcal{T}_{31} & \mathcal{T}_{32} & 0 & \mathcal{T}_{34} \\ \mathcal{T}_{41} & \mathcal{T}_{42} & \mathcal{T}_{43} & 0 \end{bmatrix}, \tag{19}$$

where

$$\mathcal{T}_{12} = \mathcal{T}_{21} = \frac{1}{8}\begin{pmatrix} -\frac{1}{2} & -\frac{3}{2} & 0 \\ -\frac{3}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{20}$$

$$\mathcal{T}_{13}=\mathcal{T}_{31}=\tfrac{1}{8}\begin{pmatrix}1&0&0\\0&-\frac{1}{2}&-\frac{3}{2}\\0&-\frac{3}{2}&-\frac{1}{2}\end{pmatrix}, \tag{21}$$

$$\mathcal{T}_{14}=\mathcal{T}_{41}=\tfrac{1}{8}\begin{pmatrix}-\frac{1}{2}&0&-\frac{3}{2}\\0&1&0\\-\frac{3}{2}&0&-\frac{1}{2}\end{pmatrix}, \tag{22}$$

$$\mathcal{T}_{23}=\mathcal{T}_{32}=\tfrac{1}{8}\begin{pmatrix}-\frac{1}{2}&0&\frac{3}{2}\\0&1&0\\\frac{3}{2}&0&-\frac{1}{2}\end{pmatrix}, \tag{23}$$

$$\mathcal{T}_{24}=\mathcal{T}_{42}=\tfrac{1}{8}\begin{pmatrix}1&0&0\\0&-\frac{1}{2}&\frac{3}{2}\\0&\frac{3}{2}&-\frac{1}{2}\end{pmatrix}, \tag{24}$$

$$\mathcal{T}_{34}=\mathcal{T}_{43}=\tfrac{1}{8}\begin{pmatrix}\frac{1}{2}&\frac{3}{2}&0\\\frac{3}{2}&-\frac{1}{2}&0\\0&0&1\end{pmatrix}. \tag{25}$$

The eigenvectors of T are easily obtained with the help of the symmetry operations of the tetrahedral point group. Table I lists these normalized eigenvectors and the corresponding eigenvalues with their multiplicity. In the same table is given the total dipole moment associated with each mode, thus showing which modes are optically active and what are the relative absorption strengths in the case of the tetrahedron cluster. In Table II, we give the *optically active* modes only and their relative strengths for the small-size aggregates which have been considered and for which the eigenvalue problem has been explicitly solved.

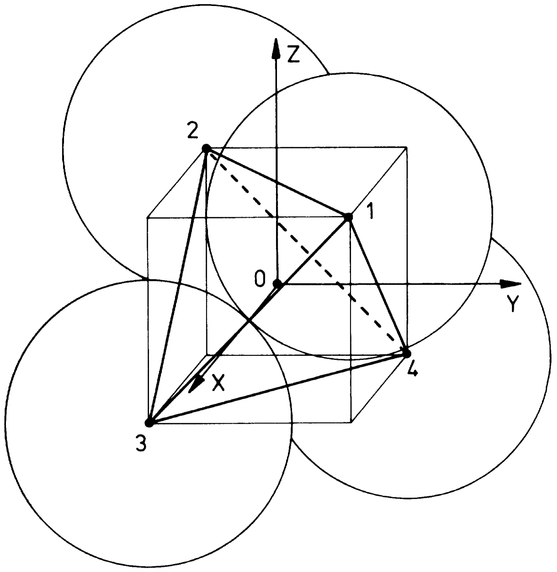


FIG. 2. Coordinate systems and positions of the ionic spheres composing a tetrahedron microcrystal.

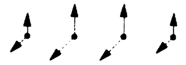
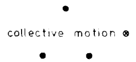
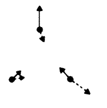
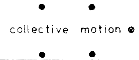
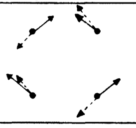
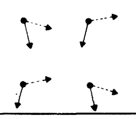
IV. LATTICE MODELS

In this section, we consider models in which a given aggregate is repeated indefinitely in one,

TABLE I. The normalized eigenvectors and the corresponding eigenvalues with their respective multiplicity for the tetrahedron microcrystal illustrated in Fig. 2. In the last column, the total dipolar moment associated with each mode is given.

Normalized eigenvectors	Eigenvalues	Multiplicity	$\left\|\sum_{i=1}^{N}\vec{q}_i^{(\mu)}\right\|^2$
$(2\sqrt{3})^{-1}(111,-1\,-1\,1,1\,-1\,-1,-1\,1\,-1)$	$\frac{5}{8}$	×1	0
$(2\sqrt{2})^{-1}(1\,-1\,0,-1\,1\,0,110,-1\,-1\,0)$ $(2\sqrt{2})^{-1}(-1\,0\,1,101,-1\,0\,-1,1\,0\,-1)$	$\frac{1}{16}$	×2	0
$(2\sqrt{2})^{-1}(1\,-1\,0,-1\,1\,0,-1\,-1\,0,110)$ $(2\sqrt{2})^{-1}(-1\,0\,1,-1\,0\,-1,101,1\,0\,-1)$ $(2\sqrt{2})^{-1}(0\,1\,-1,011,0\,-1\,1,0\,-1\,-1)$	$-\frac{5}{16}$	×3	0
$A\ (11B,-1\,-1B,-1\,1B,11B)$ $A\ (1B1,1\,B\,-1,-1\,B\,1,-1\,B\,-1)$ $A\ (B11,B\,1\,-1,B\,-1\,-1,B\,-1\,1)$ with $A=3/[2(73+\sqrt{73})]^{1/2}$ $B=\frac{1}{6}(1+\sqrt{73})$	$\frac{1}{32}(1-\sqrt{73})$	×3	2.33
$A\ (11B,-1\,-1\,B,-1\,1\,B,11B)$ $A\ (1B1,1\,B\,-1,-1\,B\,1,-1\,B\,-1)$ $A\ (B11,B\,1\,-1,B\,-1\,-1,B\,-1\,1)$ $A=3/[2(73-\sqrt{73})]^{1/2}$ $B=\frac{1}{6}(1-\sqrt{73})$	$\frac{1}{32}(1+\sqrt{73})$	×3	1.77

TABLE II. Optically active modes and their relative strengths $A^{(\mu)}$ for all the small-size aggregates which have been explicitly considered here. In the first column, letters indicate the type of aggregates: (a) pair; (b) linear triplet; (c) linear quadruplet; (d) equilateral triangle; (e) square. Vectors representing the optically active modes are indicated in the second column; multiplicities are also given. In the third column, the optical absorption $A^{(\mu)}$ relative to the single sphere absorption is given. The fourth column gives the λ_μ values.

(a)	 1×	2	− 0.250
	 2×	2	+ 0.125
(b)	 2×	0.65×10^{-1}	− 0.169
	 2×	2.93	+ 0.185
	 1×	2.93	− 0.370
	 1×	0.65×10^{-1}	+ 0.338
(c)	 1×	3.83	− 0.436
	 1×	0.16	+ 0.176
	 2×	0.72×10^{-1}	− 0.088
	 2×	3.5	+ 0.218
(d)	 1×	3	+ 0.250
	 2×	2.17	− 0.241
	 2×	0.83	+ 0.178
(e)	 1×	4	+ 0.294
	 2×	1.7	+ 0.160
	 2×	3.8	− 0.204

two, or three dimensions to form chains, planar, or three-dimensional aggregates. The calculation of the full frequency spectrum of such an infinite aggregate is a standard problem in lattice dynamics. However, here we need only the long-wavelength dipolar modes since we are interested in ir properties. In practice, the wavelength is so much larger than the particle dimension that we are justified to assume that there is an infinite number of particles within a wavelength. Then, for the optical absorption we are interested only in the modes $\vec{k}=0$ for which all spheres oscillate in phase.

The question arises whether one should include retardation effects for the calculation of the eigenmodes of infinite aggregates. The consideration of the convergence of dipole lattice sums immediately shows that this is not necessary for the linear and planar aggregate while for three-dimensional models, retardation effects are important (and well known in the problem of optical absorption of single crystals).

For a general wave vector $\vec{k}$, the eigenfrequencies are the square roots of the eigenvalues of the dynamical matrix

$$\Omega(\vec{k}) = \omega_S^2\left(E_{3n} + fR^3 {\sum_j}' T_j e^{i\vec{k}\cdot\vec{R}_j}\right), \tag{26}$$

where n is the number of spheres in the primitive cell of the sphere lattice, $\vec{R}_j$ are the lattice positions, and T_j is the $3n\times 3n$ matrix whose elements are the various n^2 dipolar tensors like

$$T_{0j,\mu\nu} = (E_3 - 3\vec{R}^0_{j\mu\nu}\vec{R}^0_{j\mu\nu})/R^3_{j\mu\nu}\,, \tag{27}$$

$\vec{R}_{j\mu\nu}$ being the distance between sphere μ in the reference cell and sphere ν in the jth cell.

For instance, for a linear single-strand chain of touching spheres ($n=1$), we have three long-wavelength, optically active modes (vanishing $\vec{k}$, parallel to the chain) illustrated and labeled 1, 2, 3 in Fig. 3. The longitudinal mode 1 is nondegenerate and has a frequency

$$\omega_1 = \omega_S\left(1 - \frac{f}{4}{\sum_j}' \frac{1}{|j|^3}\right)^{1/2}, \tag{28}$$

where j takes on all nonzero integer values. The two degenerate transverse modes have a frequency

$$\omega_2 = \omega_3 = \omega_S\left(1 + \frac{f}{8}{\sum_j}' \frac{1}{|j|^3}\right)^{1/2}. \tag{29}$$

Here again, the frequencies must be consistent with the polarizability $f(\omega)$. The solutions are given by formula (17) but with

$$\lambda_\mu = \begin{cases} -\dfrac{1}{4}\displaystyle{\sum_{j=-\infty}^{+\infty}}' \dfrac{1}{|j|^3} & \text{for } \mu = 1, \quad (30) \\ +\dfrac{1}{8}\displaystyle{\sum_{j=-\infty}^{+\infty}}' \dfrac{1}{|j|^3} & \text{for } \mu = 2, 3. \quad (31) \end{cases}$$

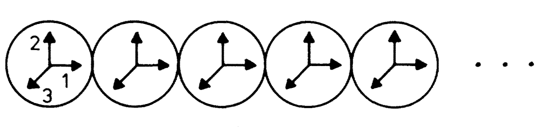


FIG. 3. Eigenvectors of the three long-wavelength optically active modes of a linear single-strand chain of touching spheres.

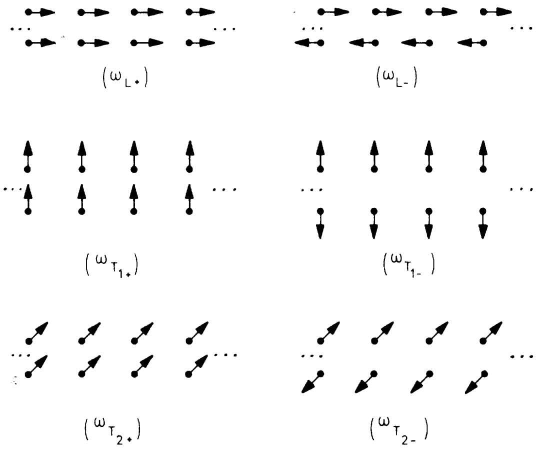


FIG. 4. Eigenvectors of the long-wavelength modes of a double strand of touching spheres. Eigenvalues having a minus index are not optically active.

We next consider the double-strand chain of touching spheres illustrated in Fig. 4. We find six long-wavelength modes, three "acoustic"-like modes which are optically active and three "optical"-like modes which are inactive (zero dipole moment per cell). The frequencies are given by formula (17) with the following λ_μ's:

$$\lambda_{L\pm}=-\frac{1}{4}\sum_{j=-\infty}^{+\infty}{}' |j|^{-3}\pm\frac{1}{8}\sum_{j=-\infty}^{+\infty}\frac{1-2j^2}{(1+j^2)^{5/2}} \tag{32}$$

(longitudinal modes);

$$\lambda_{T_1\pm}=\frac{1}{8}\sum_{j=-\infty}^{+\infty}{}' |j|^{-3}\pm\frac{1}{8}\sum_{j=-\infty}^{+\infty}\frac{j^2-2}{(1+j^2)^{5/2}} \tag{33}$$

(transverse, in-plane modes);

$$\lambda_{T_2\pm}=\frac{1}{8}\sum_{j=-\infty}^{+\infty}{}' |j|^{-3}\pm\frac{1}{8}\sum_{j=-\infty}^{+\infty}\frac{1}{(1+j^2)^{3/2}} \tag{34}$$

(transverse, out-of-plane modes). The "±" signs refer to the parity of the mode. Only the "+" modes are optically active.

In the case of a close-packed planar aggregate of spheres, the eigenvectors of the three long-wavelength active modes are illustrated in Fig. 5. The corresponding eigenvalues are given by Eq. (17) where

$$\lambda_\perp=\frac{1}{8}\sum_{i,j=-\infty}^{+\infty}{}' (i^2+j^2+ij)^{-3/2}, \tag{35}$$

$$\lambda_{\parallel 1}=\lambda_{\parallel 2}=-\tfrac{1}{2}\lambda_\perp . \tag{36}$$

Finally, we give the λ values appropriate to a three-dimensional fcc lattice of spheres[10] (neglecting retardation). There are one longitudinal and two transverse, degenerate polarization modes with

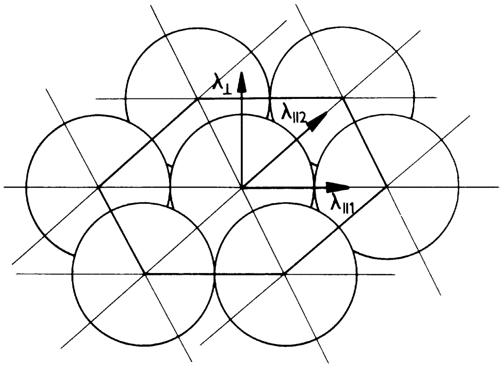


FIG. 5. Eigenvectors of the three long-wavelength active modes for a close-packed planar aggregate of spheres. Eigenvalues are given in the text.

$$\lambda_L=\tfrac{8}{3}\pi nR^3=\tfrac{1}{3}\sqrt{2}\,\pi, \tag{37}$$

$$\lambda_{T_1}=\lambda_{T_2}=-\tfrac{4}{3}\pi nR^3=-\pi/3\sqrt{2}, \tag{38}$$

where $n=4/a^3$ is the sphere number density, for a fcc lattice of cube edge a. One may compare these λ's with the extremal values 2 and −1 which generate the bulk eigenfrequencies ω_L and ω_T, respectively. One can see that a substantial (~70%) portion of the bulk interval (ω_T, ω_L) is covered by the above frequencies.

V. DISCUSSION AND CONCLUSIONS

In Table III, we have listed the frequencies corresponding to the dipole optical phonon modes of a "model NiO powder" containing one type of every aggregate considered in the previous sections. Let us note that the calculated frequencies fall on both sides of the frequency ω_S characteristic of the Fröhlich surface mode of an isolated sphere; these frequencies are distributed in the interval $\omega_T \leqslant \omega \leqslant \omega_L$, but they mainly span the upper half. One may wonder why the lower half of the spectrum is not as well represented. One reason for this is the restrictive class of clusters considered here. Although the clusters which we have studied are likely to be present in the powder, the actual statistical distribution of particles in a given sample is not known. Agglomerates more complicated than those we have considered are also present in the powder, which makes the quantitative comparison with experimental results rather difficult. A further reason why only the upper two-third of the interval (ω_T, ω_L) is covered with our aggregates is the fact that the single sphere absorption frequency ω_S is closer to ω_L than to ω_T.

TABLE III. Frequencies of ir-active modes for a powder of NiO. They are given in increasing order of ω for all the clusters considered.

ω_μ (cm^{-1})	Geometry of the aggregates
$\omega_T=401$	
477.2	fcc lattice of spheres
500.2	linear single-strand chain
502.7	double-strand chain
523.6	linear quadruplet
526.4	linear triplet
536.3	pair
537.0	equilateral triangle
537.3	tetrahedron
539.6	square
542.0	linear triplet
547.1	linear quadruplet
$\omega_S=552$	single sphere
553.5	double-strand chain
558	pair
559.7	square
560.4	equilateral triangle
560.7	linear triplet
562.1	linear quadruplet
563.4	equilateral triangle
565	square
565.2	tetrahedron
565.3	linear single-strand chain
573.6	double-strand chain
576.5	linear quadruplet
592.1	fcc lattice of spheres
$\omega_L=598$	

Micrograph pictures[1] show the presence of irregular solids, ellipsoids, chains of cube-like crystallites, etc. This variety in microcrystallite shape is also influencial for the width of the observed spectrum as shown in Ref. 5.

Indeed, from numerical calculations by Martin,[5] one finds that frequencies corresponding to edge and surface modes of cube-like solids fall in a frequency region lower than ω_S and close to ω_T. Other calculations[11] have indicated that six resonances, located in a frequency range encompassing ω_S, contribute to the optical absorption of an isolated cube. This must be contrasted with the single resonance frequency ω_S of an isolated sphere.

Whatever the shape assumed for the individual particles, it is clear from our calculations on spheres that a substantial broadening mechanism is to be found in their clustering, so that further investigations of cluster geometries and particle size distribution would be of great interest for the interpretation of experimental infrared spectra of powders.

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