Plasmon Cohesive Energy of Voids and Void Lattices in Irradiated Metals

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The contribution of the long-range electron–Coulomb correlation to the surface energy of an empty spherical cavity in a metal is calculated from the zero-point energy of surface plasmons characteristic of the spherical void boundary. At large void radii one recovers the result previously derived for a planar metal-vacuum interface. Next it is shown that, owing to the overlapping of surface-plasmon zero-point oscillations around two neighboring voids, an effective attraction exists between them which is analogous to the van der Waals (dispersion) forces between small metal spheres in vacuum. However, because of the monopole nature of the fundamental surface-plasmon mode of a void, the effective void-void interaction is much stronger and of much longer range than the attraction of spherical particles for which the lowest-order plasmon mode is of dipole type only. It is therefore proposed that plasmons may be one of the important physical processes responsible for void nucleation and growth and also for the observed occurrence of three-dimensional void arrays in some heavily irradiated transition metals. In a void lattice, the plasmon modes of an isolated void split and broaden into bands. The resulting plasmon cohesive energy per void is estimated to be of the order of -1 eV for the observed bcc void array in molybdenum and -2.5 eV for the fcc nickel array.

I. INTRODUCTION

Voids, or roughly spherical empty cavities, have been observed to form in metals subjected to large radiation doses at elevated temperatures.[1] The voids, which result from aggregation of mobile atomic vacancies generated during irradiation, generally appear randomly dispersed in homogeneously irradiated regions. However, under special experimental conditions,[2] voids can grow at regularly distributed sites, forming a three-dimensional array of extremely high spatial coherence. For instance, a bcc array was obtained in molybdenum[3] with a lattice parameter of 220 Å and an average void radius of 20 Å, the perfect order extending over many thousands of voids.

The processes of nucleation, growth, and eventual "crystallization" of voids have received a great deal of attention in recent years, owing to their intrinsic scientific interest and especially to the technological importance of the attendant volume expansion or "swelling" phenomenon. In practice, the swelling fraction, i.e., the void volume divided by the total volume, may be as high as 10% after large irradiation doses. Clearly, the amount of internal surface area introduced into such samples can be relatively very large, as compared, for instance, to the area of the external boundaries. Under such conditions, it is likely that the same physical processes which determine the fundamental nature of surface metallic cohesion are also crucially involved in the void occurrence.

Recently it has been shown[4,5] that plasmons, i.e., quantum density fluctuations of the electron-ion plasma in a metal, play an important if not a leading role in determining the surface energy of a planar metal-vacuum interface. Briefly, the creation of new surfaces, e.g., by splitting the metal into two parts along a plane, necessitates, among other things the creation of surface plasmons characteristic of the interfaces to replace an equal number of formerly bulk plasmons. The corresponding zero-point energy shift per unit area of newly created surface has been shown[4] to account quantitatively for the measured surface energies of most metallic elements. Such agreement appears to indicate that surface metallic cohesion is almost entirely of plasmon origin.

The first purpose of this paper (Sec. II) will therefore be to calculate that part of the surface energy of an empty isolated void in a metal, which is due to the existence of surface plasmons characteristic of the spherical boundary of the void, and to establish the connection with the plasmon energy of a planar interface.

Next we recall that plasmons imply the cooperative motion of valence electrons over large distances in the metal. Thus, the disturbance to the plasmon degrees of freedom caused by the presence of a void is likely to be felt at considerable distances from the void site. A consequence of the plasmon long-range coherence in the planar-surface geometry is that the surface cohesive energy includes not only the energy required to produce a microscopic gap into the bulk metal, but also the energy required to separate the two semi-infinite solids to macroscopic distances. In other words, some work has to be done against the long-range van der Waals adhesion forces which, for metals, have been shown[6] to arise from the

overlap of the surface plasmons of the two interfaces. Although small, this latter interaction energy is important for certain cohesion problems involving very small particles, such as the stability of colloidal suspensions.[7]

Once it is recognized that attractive van der Waals forces act in vacuum between small metallic particles, the idea naturally arises that similar forces should exist between empty cavities in bulk metals by virtue of a sort of reciprocity principle. In a language more appropriate to the void problem, the relevant question, from the plasmon point of view, is whether it is energetically advantageous to create a void next to an already existing one, rather than at some isolated site in the bulk metal. If such is the case, an effective attraction will exist between voids, which could contribute significantly to the occurrence of void growth and eventual ordering.

Our second purpose will be to show (Sec. III) that, even in a *completely isotropic* continuum model of a metal, voids indeed interact via the overlap of the fields of their associated surface plasmons. This purely quantum-mechanical effect may be particularly important for understanding voids, in view of the circumstance that within the framework of classical elasticity theory[8-10] there should be no interaction between voids in an isotropic elastic continuum.

In treating the problem of two interacting spheres in vacuum simultaneously with the case of a pair of voids, one discovers a fundamental difference between the dispersion forces of the two physical systems. Voids possess a surface-plasmon mode, under which the free-electron gas executes *radial* oscillations around the cavity. This electron motion induces a uniform superficial charge density on the cavity surface such that each void acts as a fluctuating *monopole* whose field extends over the full range of a bare point charge at the center. The overlapping of the monopole fields of two neighboring voids gives rise to a quantum-mechanical interaction which decreases only as the inverse *square* of the distance. In contrast, the van der Waals interaction of two spheres is well known to decrease as the inverse *sixth power* of the distance, because spheres "see" each other only through their fluctuating *dipole* (or higher-order pole) fields. A surface-monopole mode cannot exist in a solid sphere without postulating an unphysical singular source or sink of electrons at the center.

The third purpose of this work (Sec. IV) consists of an attempt to calculate the band structure of the monopole-plasmon mode in a regular array of identical voids and, from it, to obtain an estimate of the plasmon cohesive energy of the array. Difficulties arise from the divergence of lattice sums over the long-range pair interactions, so that retardation potentials and other long-range-cutoff effects have to be considered to obtain a finite cohesive energy. The result clearly indicates that plasmons should indeed play an important role in the void clustering effect, at least in providing a large contribution to the attractive part of the total cohesion.

II. ISOLATED VOID

A. Dispersion Relation

It may be useful to first briefly recall how one can obtain from Maxwell's equations the eigenmodes of surface polarization of a finite-size crystal. The metallic medium is represented by a lossless isotropic dielectric continuum with a frequency-dependent dielectric function

$$\epsilon(\omega) = 1 - \omega_p^2/\omega^2 \ , \tag{1}$$

where $\omega_p = (4\pi ne^2/m)^{1/2}$ is the bulk plasma frequency of the valence electrons. In the present section, the distances involved (void radii) are so small compared to the characteristic wavelength $\lambda_p = 2\pi c/\omega_p$ that there will be no need to take radiation effects into account by using the fully retarded Maxwell's equations. The nonretarded surface plasmons are defined as those eigenmodes of oscillations of the electric field which are both rotational- and divergence-free[11,12] and which satisfy the usual boundary conditions at the metal-vacuum interface. The modes of an ionic crystal sphere in the optical-phonon frequency range have been discussed in detail by Englman and Ruppin.[11] The plasmon modes of a metallic sphere can be deduced from their results by using a formal correspondence between optical phonons and plasmons.[13,14] For a spherical-void geometry, the method is exactly the same as for a solid sphere in vacuum: one simply replaces[15] $\epsilon(\omega)$ by $\epsilon^{-1}(\omega)$ in the continuity equation. The solutions have been studied, e.g., by Natta.[16]

The electric field is written

$$\vec{\mathbf{E}}(\vec{\mathbf{r}}) = \mathrm{grad}\left\{Y_{lm}(\theta,\phi)\left[Ar^l + Br^{-(l+1)}\right]\right\} \ , \tag{2}$$

where Y_{lm} is a spherical harmonic, and where r^l and $r^{-(l+1)}$ are linearly independent solutions of the radial Laplace equation. The arbitrary constants A and B are to be determined by conditions of regularity at the origin and at infinity, and by the continuity conditions at the surface of the sphere $r = R$. Thus, inside and outside the sphere, the fields have the respective forms

$$\vec{\mathbf{E}}_I = \mathrm{grad} AY_{lm} r^l \ , \tag{3}$$

$$\vec{\mathbf{E}}_0 = \mathrm{grad} BY_{lm} r^{-(l+1)} \ . \tag{4}$$

For a void, the boundary conditions are

$$AR^{l} = BR^{-(l+1)} \ , \tag{5}$$

$$lAR^{(l-1)} = -\epsilon(\omega)\,(l+1)\,BR^{-(l+2)} \ . \tag{6}$$

From the compatibility condition and using Eq. (1), one obtains the dispersion relation[16]

$$\omega_l = \omega_p \left(\frac{l+1}{2l+1}\right)^{1/2} \ , \quad l = 0, 1, 2, \ldots \ . \tag{7}$$

Similarly, for a solid sphere in vacuum, one finds [it suffices to replace ϵ by ϵ^{-1} in Eq. (6)]

$$\omega_l = \omega_p \left(\frac{l}{2l+1}\right)^{1/2} \ , \quad l = 1, 2, 3, \ldots \ . \tag{8}$$

These spectra are shown in Fig. 1 along with the flow patterns of the first few modes.

The $l = 0$ mode around a void, which will conveniently be called "breathing" mode, corresponds to a radially symmetrical oscillation of the electron gas. From Eqs. (3) and (4), the field inside the cavity is zero, whereas outside it is equal to the field of a point charge at the center fluctuating at the plasma frequency ω_p. This field provides the restoring force on the electrons to sustain the radial current oscillations. Although its frequency equals the bulk plasma frequency ω_p, the breathing mode nevertheless represents a surface oscillation in the sense that the fields and currents decay away from the surface, and the density fluctuations occur only at the surface (in the nonretarded limit).

In a full metallic sphere, the $l = 0$ mode would correspond to a static ($\omega = 0$) accumulation of superficial charges which can only be provided from an external source. Indeed, because of the relation $\Delta(1/r) = -4\pi\delta(\vec{r})$, no radially symmetrical current can take place without the help of an unphysical singular source of sink of electrons at the sphere center.

In general, the lth modes generate oscillating multipolar fields of order l, the range of which decreases with increasing l.

B. Surface Energy

The lth mode has the usual $2l+1$ rotational degeneracy. If $l_M \gg 1$ represents an upper bound for l, the total number of modes is approximately

$$\sum_{l=0}^{l_M} (2l+1) \simeq l_M^2 \ .$$

The value of l_M is provided by the obvious requirement that the number of zeros (or oscillations) of the angular function $Y_{l0}(\theta, \phi) = P_l(\cos\theta)$ should not exceed the number of electrons along a great circle of the sphere. Otherwise one would have surface-density fluctuations over a scale smaller than the interelectronic separation. Thus

$$l \lesssim l_M = 2\pi R/\lambda_c \equiv k_c R \ , \tag{9}$$

where λ_c is the average distance between valence electrons. It should be remarked here that the isotropic continuum approximation implicit in the use of a local dielectric function $\epsilon(\omega)$ breaks down before l reaches l_M.[11] When considering density fluctuations on an atomic scale, bulk dispersion effects, i.e., nonlocality in the dielectric function $\epsilon(\omega, \vec{k})$, should be considered. However, such dispersion

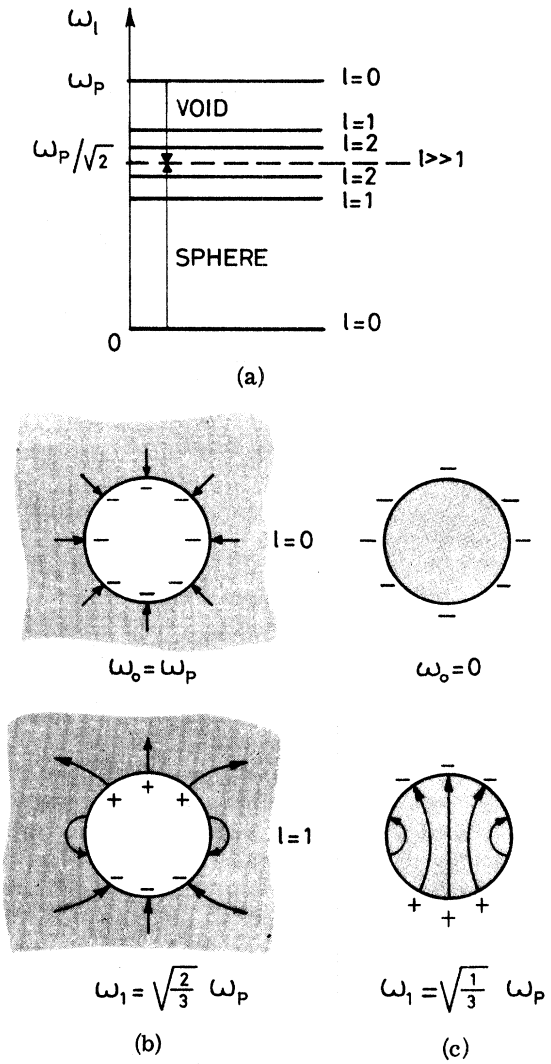

FIG. 1. (a) Spectrum of possible surface-plasmon quanta of a spherical metallic particle (lower half) and of a spherical void in a metal (upper half). The levels l are $2l+1$ degenerate. For large l, both sets converge to the common limit $\omega_p/\sqrt{2}$. The void spectrum is "peeled off" the bulk branch ω_p, whereas the sphere spectrum is "lifted out" of the zero-frequency shear branch $\omega = 0$. (b) Mode patterns of electron currents around a void corresponding to the breathing ($l = 0$) and dipole ($l = 1$) modes. The electron density remains uniform everywhere except on the surfaces, where charges accumulate as shown. (c) Same as in (b), for a full sphere. The zero-frequency $l = 0$ surface mode cannot exist without an external singular source or a sink of electrons at the sphere center.

will only affect the finer details of the surface cohesion energy, such as its dependence on the crystallographic orientation of the interface.

When a cavity is created in the bulk material by removing a metallic sphere, both sets of void and sphere modes (7) and (8) are created at the expense of an equal number of formerly bulk modes. This is a consequence of the so-called "Bergrenzung" sum rule,[4,14] which demands that the total number of collective degrees of freedom should remain unaffected by the introduction of new boundaries. It is already apparent in Fig. 1 that the set of cavity modes (7) drops, so to speak, from the bulk branch at ω_p, whereas the set of sphere modes (8) is lifted out of a zero-frequency branch $\omega = 0$. This can be shown rigorously for the present spherical geometry in the same manner as it has been established for the slab geometry somewhere else.[14] This redistribution of degrees of freedom results in a shift of zero-point plasmon energy

$$\sigma = \sum_{l=0}^{l_M} \frac{1}{2}\hbar\,(\omega_l^{\text{void}} + \omega_l^{\text{sph}} - \omega_p)\,(2l+1) \quad . \tag{10}$$

If the sphere radius R is much larger than the atomic lattice parameter, i.e., if $l_M \gg 1$, one can replace all ω_l's in (10) by their common asymptotic value $\omega_p/\sqrt{2}$. Then Eq. (10) reduces to

$$\sigma \simeq \tfrac{1}{2}\hbar\omega_p\,(\sqrt{2}-1) l_M^2 \quad . \tag{11}$$

Since *two* spherical surfaces are produced (the void and the extracted sphere), the surface energy per unit area is

$$\sigma_{\text{LR}} \equiv \sigma/8\pi R^2 = (1/16\pi)\,(\sqrt{2}-1)\hbar\omega_p k_c^2 \quad , \tag{12}$$

which coincides with the result previously obtained for the planar metal-vacuum interface.[4] It has been shown[4] that this extremely simple formula accounts surprisingly well for the surface cohesion of most metals. The quantitative prediction of the surface energies of more than 50 metallic elements on the basis of this simple theory strongly suggests that surface metallic cohesion is almost entirely of plasmon origin.

One might extrapolate the result (10) to the limit of small void radii, bearing in mind, however, that this formula is strictly valid only for a continuum dielectric. For instance, if one takes $l_M = 1$ to simulate the case of a single atomic vacancy, one finds the absurd result that the plasmon formation energy of a vacancy-interstitial pair should be

$$W_v = \tfrac{1}{2}\hbar\omega_p 3(\sqrt{\tfrac{2}{3}} + \sqrt{\tfrac{1}{3}} - 1) \simeq 10 \text{ eV} \quad .$$

This overestimation clearly arises from the neglect of dispersion effects at very short wavelength. The problem of plasmon behavior around an aggregation of a small number of vacancies would be better formulated as a problem of dynamical screening of a localized charge inhomogeneity. In view of the rather large value of the basic plasmon quantum $\hbar\omega_p$, even small modifications in the plasmon density of states (e.g., by the appearance of localized plasmon modes around the defect[17]) are likely to result in a non-negligible dynamical contribution to the formation energy of the vacancy or vacancy cluster.

C. Void Hamiltonian

It will prove useful to rederive the frequency of the breathing mode directly from Newton's law. An electron at distance r from the cavity center is acted upon by the field of a superficial charge $\sigma(t)$ which, at time t, has been accumulated on the sphere by a radial fluctuation. If $x(r, t)$ is the collective electron radial displacement, its equation of motion is

$$m\,\ddot{x}(r, t) = -\sigma(t) e/r^2 \quad . \tag{13}$$

The surface charge $\sigma(t)$ must satisfy a flux conservation or continuity equation[18]

$$\sigma(t) = 4\pi r^2 ne\, x(r, t) \quad , \tag{14}$$

where ne is the bulk electron density. Substitution of (14) into (13) yields the desired result

$$\ddot{x} + \omega_p^2 x = 0 \quad . \tag{15}$$

The Hamiltonian of the breathing mode is therefore

$$h_0 = \int d\vec{r}\, n \tfrac{1}{2} m\,(\dot{x}^2 + \omega_p^2 x^2) \tag{16}$$

$$= \tfrac{1}{2} 4\pi nm \int_R^\infty dr\, r^2 (\dot{x}^2 + \omega_p^2 x^2) \quad . \tag{17}$$

By using the relationship (14), one finds

$$h_0 = (1/2R\omega_p^2)\,(\dot{\sigma}^2 + \omega_p^2 \sigma^2) \quad . \tag{18}$$

In a similar fashion, one can establish the free Hamiltonian of the dipolar modes. If $\vec{p}$ designates the dipolar moment of the surface-density fluctuation, one has

$$h_1 = (1/2R^3\omega_1^2)\,(\dot{\vec{p}}^2 + \tfrac{2}{3}\omega_p^2 \vec{p}^2) \quad . \tag{19}$$

In general, the free Hamiltonian on the lth mode is

$$h_l = \frac{1}{2R^{2l+1}\omega_l^2} \sum_{m=-l}^{+l} (\dot{q}_{lm}^2 + \omega_l^2 q_{lm}^2) \quad , \tag{20}$$

where the q_{lm} are the multipolar moments of order l.

III. SMALL VOID CLUSTERS

A. Pair of Voids

We now consider the main problem of this paper, which is to determine the plasmon cohesive energy of two voids. This quantity is defined as the difference between the energies required to create

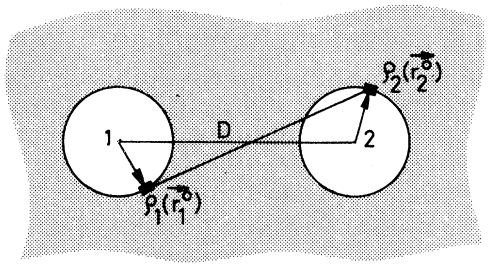

FIG. 2. Two identical voids at finite distance D of each other. A surface-charge-density fluctuation developing on void 1 will be felt on void 2 through the Coulomb interactions between the local surface charge densities $\rho_1(\vec{r}_1^{\circ})$ and $\rho_2(\vec{r}_2^{\circ})$.

two neighboring voids and two isolated voids. When two voids are within a finite distance D of each other (Fig. 2), the fluctuating fields associated with each plasmon mode ω_l overlap and interact, so that all mode frequencies will be shifted. The cohesive energy defined above will be given by the total shift in zero-point energy of all modes. We have here a situation quite similar to the formation of a diatomic molecule. A convenient approach to study the plasmon energy levels of the void system is the Hamiltonian formalism started in Sec. II C. Our first task is to write down the void-void interaction Hamiltonian in terms of the multipolar moment operators q_{lm} of each separated void. The interaction potential is clearly (see Fig. 2)

$$V(D)=\frac{1}{(4\pi)^2}\int\int d\vec{r}_1^{\circ}d\vec{r}_2^{\circ}\,\frac{\rho_1(\vec{r}_1^{\circ})\,\rho_2(\vec{r}_2^{\circ})}{|\vec{r}_2-\vec{r}_1|}\ , \qquad (21)$$

where the superscript $\circ$ means that the vector is restricted to the surface of the void. The integrals are over the two sphere surfaces, and ρ_1 and ρ_2 represent local superficial charge densities induced by a general electron-surface-density fluctuation around the voids. Assuming that $D \gg R$, one can expand the integrand in powers of R/D, using

$$\frac{1}{|\vec{r}_2-\vec{r}_1|}=\frac{1}{D}+\frac{\vec{D}}{D^2}\cdot(\vec{r}_2-\vec{r}_1)+\vec{r}_1\cdot\frac{E-3\vec{D}^{\circ}\vec{D}^{\circ}}{D^3}\cdot\vec{r}_2+\cdots\ , \qquad (22)$$

where E is the 3×3 unit matrix.

Introducing the multipole moments of the surface-charge distribution

$$\int d\vec{r}_1^{\circ}\rho_1(\vec{r}_1^{\circ})=4\pi\sigma_1\ , \qquad (23)$$

$$\int d\vec{r}_1^{\circ}\,\vec{r}_1\rho_1(\vec{r}_1^{\circ})=4\pi\vec{p}_1\ , \qquad (24)$$

etc., one finds

$$V(D)=\frac{\sigma_1\sigma_2}{D}+(\sigma_1\vec{p}_2-\sigma_2\vec{p}_1)\cdot\frac{\vec{D}^{\circ}}{D^2}+\vec{p}_1\cdot\frac{E-3\vec{D}^{\circ}\vec{D}^{\circ}}{D^3}\cdot\vec{p}_2+\cdots\ . \qquad (25)$$

The first term is the monopole-monopole coupling of the two breathing modes of the voids. The second term couples the breathing mode of each void with the dipole mode of the other, while the third term gives the dipole-dipole interaction, etc.

Since the void concentrations are such that

$$\rho\equiv R/D\ll1\ , \qquad (25)$$

we shall limit the Hamiltonian to the dipole-dipole terms. Note that $V(D)$ couples the breathing modes only to the component of the dipole modes along the molecular void axis, i.e., the $m=0$ dipolar plasmon. In general, only multipolar plasmons of same m couple together, since m remains a good "quantum" number as a result of rotational invariance around the void axis. Introducing the compact notation

$$q=\left(\sigma_1,\ \sigma_2,\ \frac{p_1}{R},\ \frac{p_2}{R}\right), \qquad (26)$$

where p_1 and p_2 are the $m=0$ dipolar moments, the Hamiltonian of the coupled voids has the form

$$H=(1/2R\omega_p^2)\,(\dot{q}^2+q\cdot\Omega^2\cdot q)+H_m\ , \qquad (27)$$

where

$$\Omega^2=\omega_p^2\begin{pmatrix}1 & \rho & 0 & \rho^2\\ \rho & 1 & -\rho^2 & 0\\ 0 & -\rho^2 & \frac{2}{3} & -2\rho^3\\ \rho^2 & 0 & -2\rho^3 & \frac{2}{3}\end{pmatrix}\ , \qquad (28)$$

and where H_m is the interaction Hamiltonian of the $m=\pm1$ dipole plasmons which do not couple to the breathing modes. The secular equation of the dynamical matrix Ω^2 is easily found to be

$$(\lambda^2-1)\,(\lambda^2-\tfrac{2}{3})=\pm[\rho(\tfrac{2}{3}-\lambda^2)-\rho^3(1-\lambda^2)]\ , \qquad (29)$$

and the four roots are

$$\lambda^2\equiv\omega^2/\omega_p^2=\tfrac{1}{2}\left(\tfrac{5}{3}\pm\rho(1-\rho^3)\right.$$
$$\left.\pm\{[\tfrac{5}{3}\pm\rho(1-\rho^3)]^2-4[\tfrac{2}{3}+(\tfrac{2}{3}\rho-\rho^3)]\}^{1/2}\right)\ . \qquad (30)$$

It turns out that the breathing modes $\lambda^2=1$ are modified to order ρ, whereas the dipole modes $\lambda^2=\frac{2}{3}$ are affected only to order ρ^3. There is no frequency shift of order ρ^2.

If one neglects the ρ^3 terms in (29), the solutions (30) reduce to

$$\lambda=\sqrt{\tfrac{2}{3}}\qquad\text{(twice)} \qquad (31)$$

$$=(1\pm\rho)^{1/2}\ , \qquad (32)$$

as is obvious from the matrix Ω^2 itself. Since in

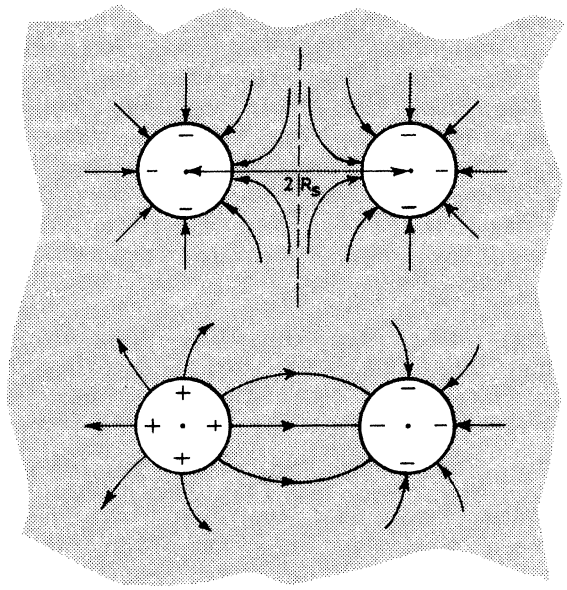

FIG. 3. Current patterns and surface charge densities associated with the symmetrical (above) and antisymmetrical (below) breathing modes of surface-plasmon oscillations around two neighboring voids.

practice the value of ρ is of order $\rho \simeq 10^{-1}$, we shall limit ourselves to the consideration of interacting breathing modes only. The reason we have written the Hamiltonian (25) up to ρ^3 terms is to point out that, in the case of two neighboring metallic spheres in vacuum, only the third term (and higher-order terms) of this expansion exists, so that the lowest-order frequency shifts are of order ρ^3 in this case.

The harder frequency $\omega_+ = \omega_p(1+\rho)^{1/2}$ in (32) corresponds to the two voids "breathing" in phase, while the softer mode $\omega_- = \omega_p\ (1-\rho)^{1/2}$ involves an antisymmetric breathing. Clearly, the latter mode is the bonding (collective) orbital, whereas the former is the antibonding orbital (see Fig. 3). There is, however, no net binding of order ρ, because the average monopole on each void is zero. Only the average square of the quantum fluctuations does not vanish as a result of the uncertainty principle. The cohesive energy of the pair is

$$W(D) = \tfrac{1}{2}\hbar[\mathrm{Tr}\Omega(D) - \mathrm{Tr}\Omega(\infty)] \tag{33}$$

$$\simeq \tfrac{1}{2}\hbar\omega_p[(1+\rho)^{1/2} + (1-\rho)^{1/2} - 2] \tag{34}$$

$$= -\tfrac{1}{8}\hbar\omega_p\rho^2 \ . \tag{35}$$

Numerically, for $\rho \sim 0.1$, this amounts to $W \simeq -0.03$ eV, when using $\hbar\omega_p \simeq 25$ eV, a typical value of the plasmon quantum in transition metals.

More important is the enormous range of the pair interaction energy, since it decreases only as the inverse square of the void separation D.

In contrast, the dispersion energy of a pair of metallic spheres will depend on the inverse sixth power of their distance, since the frequencies are only shifted to order ρ^3. One should keep in mind however, that the above treatment does not include the retardation of the fluctuating electromagnetic fields. Retardation effects will become appreciable when D becomes comparable to the wavelength $\lambda_p = 2\pi c/\omega_p$ ($\simeq 500$ Å in transition metals). A fluctuation occurring on the surface of void 1 at time t is not felt on the surface of void 2 before the time $t + D/c$. If $D \gtrsim \lambda_p$, the field of the fluctuation will be substantially out of phase with the equivalent fluctuation of void 2, and partial cancellation will result. Although we have not attempted to study the radiation effects in detail, we shall simply take them into account by replacing (35) by the law

$$W(D \gtrsim \lambda_p) \simeq -\tfrac{1}{8}\hbar\omega_p\rho^2\lambda_p/2D \tag{36}$$

on the grounds that such a reduction factor $\lambda_p/2D$ occurs between pairs of atoms[19] or solid metallic spheres (which amount to "atoms" of polarizability R^3) as well as between triplet of atoms.[19]

B. Three- and Four-Voids Clusters

A further important property of the dispersion energy of the monopole type is its nonadditivity with respect to the number of voids. If one considers an equilateral triplet of voids, the matrix to be diagonalized is

$$\Omega^2 \simeq \omega_p^2 \begin{pmatrix} 1 & \rho & \rho \\ \rho & 1 & \rho \\ \rho & \rho & 1 \end{pmatrix} , \tag{37}$$

and the eigenvalues are

$$\lambda^2 = \begin{cases} 1+2\rho \\ 1-\rho \ \text{(twice)} \ . \end{cases} \tag{38}$$

The cohesive energy of the triplet is therefore

$$W(D) = \tfrac{1}{2}\hbar\omega_p[(1+2\rho)^{1/2} + 2(1-\rho)^{1/2} - 3] \ , \tag{39}$$

or

$$W(D) \simeq \hbar\omega_p[\tfrac{3}{8}\rho^2 + O(\rho^3)] \ , \tag{40}$$

where the first term is simply the interaction energy (35) of the three pairs of the triplet, and $O(\rho^3)$ are nonadditive contributions which may become quite large at short distances.

The case of a regular tetrahedron of identical voids is also exactly soluble and involves the dynamical matrix

$$\Omega^2 = \omega_p^2 \begin{pmatrix} 1 & \rho & \rho & \rho \\ \rho & 1 & \rho & \rho \\ \rho & \rho & 1 & \rho \\ \rho & \rho & \rho & 1 \end{pmatrix} ,$$

whose eigenvalues are

$$\lambda^2 = \begin{cases} 1+3\rho \\ 1-\rho \quad \text{(thrice)} \end{cases} .$$

The cohesive energy is approximately given by the sum of the six pair interactions of the cluster:

$$W(D) \simeq -\hbar\omega_p[\tfrac{6}{8}\rho^2 + O(\rho^3)] \ . \qquad (40')$$

By comparing (32), (38), and (40'), one sees that the hardening of the totally symmetric mode increases rapidly with the size of the void cluster, while the softening of the antisymmetric modes remains constant for these particular clusters.

Finally, we close this section by remarking that Eq. (27) does not provide the exact Hamiltonian of the void system, but only what is believed to be a good approximation when ρ is sufficiently small. The reason can be seen from our derivation of the "free"-void Hamiltonian (16) and (17). In fact, with a void cluster there is no "free" void anymore, because the electron collective displacements $\vec{x}(\vec{r}, t)$ and velocities $\dot{\vec{x}}(\vec{r}, t)$ concern all voids simultaneously. In other words, when calculating the integral (16) for a void, a small exclusion volume should be introduced for all neighboring cavities in order to avoid counting nonexisting currents inside the cavities.

Physically, one expects that such corrections should be fairly small for a pair of distant voids, because in this case, one excludes a very small portion of the integration space. In three-dimensional arrays, however, this could have a more substantial "quenching" effect in the sense that all voids have to "breathe" the same electron gas. More about this point will be said in Sec. IV.

IV. VOID ARRAY

A. Solid-Sphere Array

In this section we consider only the overlapping between the lowest-order pole modes of the array. To have a familiar system with which to compare the cohesion of a void lattice, let us first briefly indicate what one would find for a lattice of solid metallic spheres. Although the latter problem does not seem to have been explicitly studied in the literature, we can immediately obtain the solution by recalling that (i) a small metallic sphere of radius R behaves, in an external field, as an "atom" of static polarizability R^3,[15] (ii) the lowest dipole mode of a sphere has frequency $\omega_1 = \omega_p\sqrt{\frac{1}{3}}$, and (iii) the case of an fcc or hcp lattice of polarizable harmonic-point oscillators has been extensively studied.[20,21] The Hamiltonian of the sphere lattice $(\vec{R}_i)$ is written

$$H_s = \frac{1}{2\omega_1^2 R^3}\sum_i (\vec{p}_i^{\,2} + \omega_1^2 \vec{p}_i^{\,2})$$

$$+ \frac{1}{2}\sum_{ij}{}' \vec{p}_i \cdot \frac{E - 3\vec{R}^{\circ}_{ij}\vec{R}^{\circ}_{ij}}{R^3_{ij}} \cdot \vec{p}_j \ , \qquad (41)$$

and the plasmon "band structure" is found to be given by the eigenvalues of the matrix

$$\Omega(\vec{k}) = \omega_1 \left(E + R^3 \sum_j{}' \frac{E - 3\vec{R}^{\circ}_{ij}\vec{R}^{\circ}_{ij}}{R^3_{ij}} \ e^{i\vec{k}\cdot\vec{R}_{ij}}\right)^{1/2}, \qquad (42)$$

where $\vec{k}$ is a wave vector inside the first Brillouin zone B of the array structure. This formula, which immediately follows from elementary band-structure theory or from lattice dynamics, has been discussed elsewhere[21] in detail. Here we shall use only the long-wavelength approximation of it,[21] namely,

$$\lim_{\vec{k}\to 0}\Omega(\vec{k}) = \omega_1 \begin{pmatrix} (1+\frac{2}{3}z)^{1/2} & 0 & 0 \\ 0 & (1-\frac{1}{3}z)^{1/2} & 0 \\ 0 & 0 & (1-\frac{1}{3}z)^{1/2} \end{pmatrix}, \qquad (43)$$

which applies to all three cubic structures. The parameter z is given by

$$z = 4\pi N R^3 \ , \qquad (44)$$

where N is the sphere number density. The plasmon energy of the lattice per unit volume is

$$W = \tfrac{1}{2}\hbar[1/(2\pi)^3] \int_B d\vec{k}[\mathrm{Tr}\Omega(\vec{k}, N) - \mathrm{Tr}\Omega(\vec{k}, 0)]$$

$$\simeq \tfrac{1}{2} N\hbar\omega_1[(1+\tfrac{2}{3}z)^{1/2} + 2(1-\tfrac{1}{3}z)^{1/2} - 3] \ . \qquad (45)$$

To lowest order in z, the cohesive energy per sphere is thus

$$W_s = -\tfrac{1}{2}\hbar\omega_1 \tfrac{1}{12} z^2 \ . \qquad (46)$$

Using the lattice parameter appropriate to the observed molybdenum array, namely, $D = 220$ Å and $R = 20$ Å, one obtains, for a bcc lattice $z = 4\pi(2/D^3) \times R^3 \simeq 0.025$, and hence

$$W \simeq 4\times 10^{-4} \text{ eV}, \qquad (47)$$

a negligible value compared, e.g., to room temperature kT. However, if one takes $R/D \simeq 0.5$ corresponding to touching (but insulated) spheres in a bcc array, one has $z \simeq 2.5$ and the cohesion is increased to $W_s \simeq -5$ eV. It is interesting to note that in this latter example the frequency $\omega_1(1-\frac{1}{3}z)^{1/2}$ of the long-wavelength transverse mode is almost softened to zero.

B. Void Array

Let us now study the following model Hamiltonian of a void lattice:

$$H_v = \frac{1}{2\omega_p^2 R}\sum_i (\dot{\sigma}_i^2 + \omega_p^2\sigma_i) + \frac{1}{2}\sum_{ij}{}' \frac{\sigma_i\sigma_j}{R_{ij}} \ , \qquad (48)$$

where only the breathing modes have been included.

Formal calculation of the plasmon band structure is again straightforward, and one finds

$$\omega(\vec{k}) = \omega_p \left(1 + R \sum_j{}' \frac{e^{i\vec{k}\cdot\vec{R}_{ij}}}{R_{ij}}\right)^{1/2} \quad . \tag{49}$$

First, assume that the term proportional to R is small compared to 1, so that one can expand the square root in powers of $\rho = R/D$. The cohesive energy per unit volume is then

$$W = \tfrac{1}{2}\hbar[1/(2\pi)^3] \int_B d\vec{k}[\omega(\vec{k}) - \omega_p] \tag{50}$$

$$\simeq -\tfrac{1}{16}\hbar\omega_p N R^2 \sum_j{}' R_{ij}^{-2} \quad , \tag{51}$$

where we have repeatedly used the identity

$$[1/(2\pi)^3] \int_B d\vec{k}\, e^{i\vec{k}\cdot\vec{R}_j} = N\delta_{\vec{R}_j 0} \quad . \tag{52}$$

There are no linear terms in ρ in (51) because in the lattice sums $\sum_j'$, the self-energy terms $j = i$ are excluded. The result (51) is just the summation over the pair interaction energies as given by Eq. (35). One faces the difficulty that the energy per void

$$W_v \equiv W/N = -\tfrac{1}{16}\hbar\omega_p R^2 \sum_j{}' R_{ij}^{-2} \tag{53}$$

diverges when summed over an infinite void lattice. One should now introduce long-range-cutoff effects, such as the retardation potential and/or damping of the plasmon fluctuations. To do this, let us divide the environment of a given void by three nested spheres (Fig. 4): (i) an immediate neighborhood of radius R_d, where the lattice summation (53) will have to be effected over discrete lattice sites, but outside of which the summation can be approximated by continuous integration; (ii) a retardation sphere of radius $R_r \simeq \lambda_p$ outside of which the R_{ij}^{-2} law will be replaced by the R_{ij}^{-3} behavior of the pair potential (36); and (iii) the sample radius R_s inside of which the voids have developed. One obtains

$$W_v = -\tfrac{1}{16}\hbar\omega_p R^2 \left[\sum_{R_j < R_d}{}' R_j^{-2} + 4\pi N(\lambda_p - R_d) + 4\pi N \tfrac{1}{2}\lambda_p \ln(Rs/\lambda_p)\right] \quad . \tag{54}$$

In a bcc array of lattice constant D, there are 8 sites at distance $\frac{1}{2}(\sqrt{3})D$ from the reference site, 6 sites at D, 12 sites at $(\sqrt{2})D$, and 24 sites at $\frac{1}{2}(\sqrt{11})D$. This gives a discrete lattice sum that has 50 terms and that amounts to $\sum'_{R_j<R_d} \simeq 30D^{-2}$. Beyond $R_d = D[(3/8\pi)\,50]^{1/3}$, we integrate.

With $\lambda_p \simeq 500$ Å, $\rho = R/D \simeq 0.1$, and $R_s \simeq 1\ \mu$, the end result is

$$W_v = -\tfrac{1}{16}\hbar\omega_p \rho^2[40 + 25 \ln(R_s/\lambda_p)] \simeq -2 \text{ eV} \quad . \tag{55}$$

Note that the expression (54) is still divergent for large R_s and is also shape dependent. Another long-range cutoff is needed which will naturally arise from the damping of surface plasmons or, equivalently, from the damping of electron currents by electron-hole pair excitations. Thus the result (55) is to be taken only as a qualitative indication of the truly large value of the plasmon cohesive energy per void, as compared to room temperature or even to high irradiation temperature kT. Another reason for not trusting (55) as an absolute result is that the initial assumption leading to it is not valid: The dispersion relation (49) cannot be expanded in powers of ρ, especially for small values of $\vec{k}$. For $k \ll D^{-1}$, the 50 close neighbors considered above already harden the long-wavelength breathing frequency to $\omega(\vec{k} \simeq 0) \simeq (\sqrt{5})\omega_p$. Even with long-range-cutoff factors, the bandwidth may still be larger than ω_p, in which case no expansion in powers of ρ would converge. Only for $\vec{k}$ values close to the Brillouin-zone limits will the lattice sum in (49) converge relatively fast. For instance, for $\vec{k} = (2\pi/D)\ (1, 1, 1)$, i.e., at point P of the fcc Brillouin zone, the exact frequency (neglecting retardation) is given by

$$\omega(k_p) = \omega_p[1 - (R/R_0)\,\alpha_M]^{1/2} \quad , \tag{56}$$

where

$$\alpha_M = \sum_j{}' (\pm 1) R_0/R_j = 1.7627 \tag{57}$$

is the Madelung "energy"[13] of a bcc diatomic ionic lattice of nearest-neighbor distance $R_0 = \frac{1}{2}(\sqrt{3})D$. That is, for the molybdenum array,

$$\omega(k_p) = \omega_p\,(1 - 0.2)^{1/2} \simeq 0.9\omega_p \quad . \tag{58}$$

The full band structure in the [111] direction is

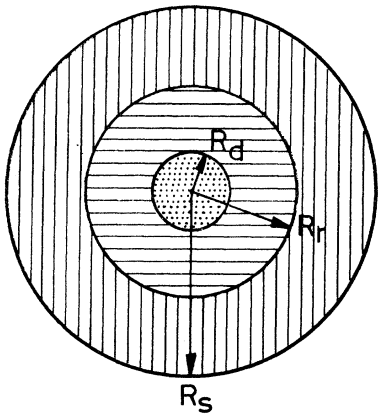

FIG. 4. Illustration of the method of calculating the lattice sums involved in the plasmon band structure of a void lattice. Inside the inner spherical region of radius R_d around the reference void, the lattice sums are performed over the discrete void sites. Outside R_d, the summations are replaced by integrations. Outside the retardation sphere $R_r \simeq \lambda_p$, the pair potentials are replaced by retarded interactions. R_S is the dimension of the region occupied by the void array.

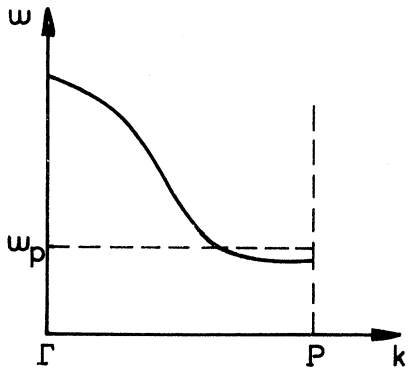

FIG. 5. Schematic band structure of the breathing plasmon of a bcc void lattice along the Λ axis.

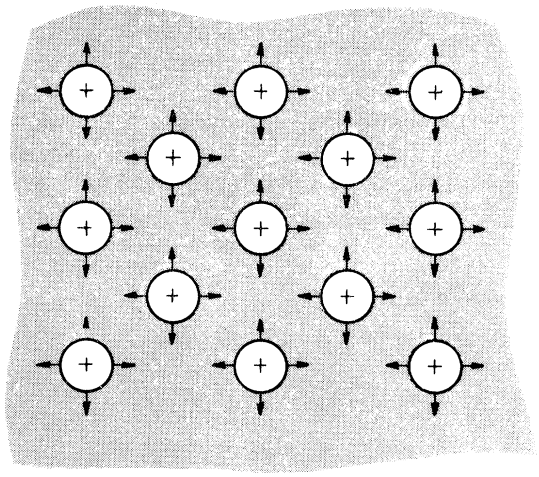

FIG. 6. Mode pattern of the long-wavelength breathing mode in a bcc void lattice. The plane of the figure is the [110] plane.

schematized in Fig. 5 (see Sec. IV C) and the mode patterns at $\vec{k} \simeq 0$ and $\vec{k}_P$ are shown in Figs. 6 and 7, respectively.

The mode at $\vec{k}_P$ consists of the two imbricated simple cubic arrays of voids breathing in opposition of phases, whereas in the $\vec{k} = 0$ modes all voids breath in phase. Clearly the former mode is strongly bonding, because for each half-period of plasma oscillations, the fluctuating charge distribution is equivalent to the arrangement of point charges in a bcc diatomic ionic crystal such as CsCl. Most modes having their $\vec{k}$ close to the Brillouin-zone faces $\vec{k}_B$ will similarly be bonding "collective" orbitals for the voids, whereas the modes near the center $\vec{k} = 0$ will be antibonding. Although the hardening of $\vec{k} \simeq 0$ modes is much larger than the softening of the $\vec{k}_B$ modes, a net binding energy nevertheless results because the phase-space factor in the k integral favors the bonding modes. Does this remain valid for increasing swelling fraction, or does a value of ρ exist above which the repulsion dominates over the attraction? If we look for an extremum of the function $W(\rho)/N$ giving the cohesive energy per void, we have to find a swelling ratio $\rho \neq 0$ such that

$$\frac{\partial}{\partial \rho}\left(\frac{W(\rho)}{N}\right) \propto \int_B d\vec{x}\,[\lambda(\vec{x}) - 1/\lambda(\vec{x})] = 0 \ , \qquad (59)$$

where we have used the reduced notations

$$\vec{k} = (2\pi/D)\,\vec{x}, \quad \vec{R}_j = D\vec{\rho}_j, \quad \omega(\vec{k}) = \omega_p \lambda(\vec{k}) \ , \qquad (60)$$

$$\lambda(\vec{x}) = 1 + \rho \sum_j{}' \frac{e^{2\pi i \vec{x}\cdot\vec{\rho}_j}}{\rho_j} \, F(\rho_j) \ , \qquad (61)$$

and where $F(\rho_j)$ is some appropriate convergence factor due to retardation and other effects. In other words, is there a nonzero swelling fraction or void density for which the average surface-plasmon breathing frequency is equal to the average of its inverse? Although this may very well be possible already with a function having a structure such as (61), it does not seem worthwhile to attempt verifying it by a detailed calculation of the full band structure in the present model. The first reason is that the actual band structure appears to be quite sensitive to the convergence function $F(\rho_j)$ which, at the present stage, is not known with sufficient accuracy. The second reason has already been mentioned at the end of Sec. III B, and stems from the fact that the initial model Hamiltonian (41) breaks down at higher void density or swelling fraction. In this model system, the free-void Hamiltonians have been written as though each void had the whole of the electron gas available around it for sustaining its own breathing. In fact, when the voids come close together, the common electron gas is to be shared between all voids, ac-

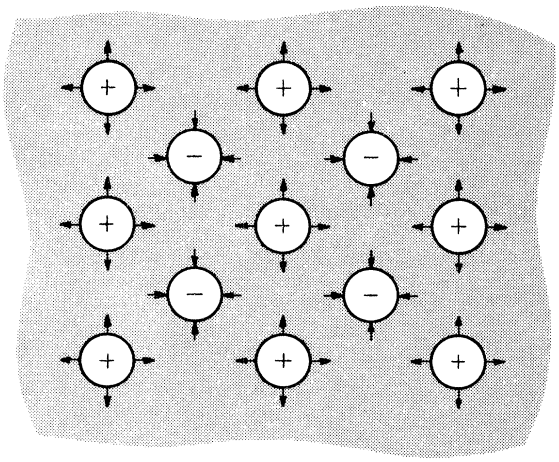

FIG. 7. Mode pattern for the principal symmetry point P of the Brillouin zone.

cording to a single continuity equation. Intuitively, one can easily see that the $\vec{k} \simeq 0$ modes will be very sensitive to this constrain, whereas the $\vec{k}_B$ modes should remain essentially unaffected for the simple reason that in this case, the electrons used up by the breathing of a void are provided by nearest-neighbor voids so that only fairly local electron currents need be involved. Such a differential quenching effect on the antibonding modes could help stabilize the void array to an optimum lattice parameter D.

C. Model Band Structure

In order to obtain a fair estimate of the actual plasmon cohesive energy of the void array, we shall now construct a model plasmon band structure, taking into account as much of the information gained in Secs. IV A and IV B as possible.

First, we have an exact *sum rule*, independent of the nature of the void-void interaction:

$$\int d\vec{x}\,[\lambda^2(\vec{x}) - 1] = 0 \ , \tag{62}$$

which results from (52) and expresses the fact that the time average (or ground-state average) of the interaction is zero. Second, we have obtained in Eq. (56) a reliable estimate of one of the most bonding modes, at point P of the Brillouin-zone limit. We shall assume a completely isotropic band structure $\lambda(x)$, independent of the direction of the wave vector. Then, a third condition is the vanishing of the derivative of $\lambda(x)$ at the Brillouin-zone edge, which here is the sphere $x = 1$.

Thus, the energy per void is

$$W_v = \tfrac{3}{2}\hbar\omega_p \int_0^1 x^2 dx\,[\lambda(x) - 1] \ , \tag{63}$$

where $\lambda(x)$ satisfies

$$\int_0^1 x^2 dx\,[\lambda^2(x) - 1] = 0 \ , \tag{64}$$

$$\lambda(1) \equiv \lambda_1 = [1 - (R/R_0)\,\alpha_M]^{1/2} \ , \tag{65}$$

$$\left[\frac{\partial \lambda(x)}{\partial x}\right]_{x=1} = 0 \ . \tag{66}$$

If we expand $\lambda^2(x)$ in the form (see Fig. 5)

$$\lambda^2(x) = 1 + \Delta - ax^2 + bx^4 \ , \tag{67}$$

the three conditions (64)–(66) determine the parameters Δ, a, and b to be

$$\Delta = \tfrac{27}{8}(1 - \lambda_1^2), \quad a = 2b = \tfrac{35}{4}(1 - \lambda_1^2) \ , \tag{68}$$

and the energy per void is then

$$W_v \simeq -\tfrac{3}{2}\hbar\omega_p \tfrac{1}{8}\left(\tfrac{1}{3}\Delta^2 - \tfrac{9}{35}\Delta a + \tfrac{74}{693}a^2\right) \tag{69}$$

up to terms of order $(R/R_0)^2$. Using the value of $\lambda_1^2 \simeq 0.8$ indicated in Eq. (58), one finally obtains

$$W_v \simeq -0.8 \text{ eV} \ . \tag{70}$$

It is particularly satisfying that this result is of the same order of magnitude as the value of -0.5 eV recently calculated by Tewary and Bullough[10] on the basis of anisotropic elasticity theory.

The same model can be applied to the fcc void array observed in Nickel[2] with the following parameters: $D = 660$ Å and $R \simeq 100$ Å. From Eq. (56), using the fcc Madelung constant $\alpha_M \simeq 1.75$, one finds $\lambda_1^2 \simeq 0.63$ at point L of the bcc Brillouin zone. The resulting plasmon cohesion (69) is found to be $W_v \simeq -2.5$ eV.

V. CONCLUSIONS

We have presented an elementary theory of plasmon effects on the surface cohesion of isolated voids, cluster of voids, and void arrays in metals. The description is macroscopic insofar as no other assumption that the applicability of a continuum (local) dielectric function (1) has been made. However, the theory is microscopic in the sense that it concerns the electronic collective degrees of freedom of the system, and it is quantum mechanical because the notion of plasmon zero-point energy has no classical analog. The fact that the host matrix is metallic is taken explicitly into account from the beginning through the use of a metallic-type dielectric function, and the particular metal is specified only by choosing the appropriate plasma frequency ω_p.

The main result of the study indicates that plasmon cohesion of voids is very strong and of extremely long range. The high perfection of the void arrays appears to involve both these characteristics of the effective void interaction. A strong void interaction is also likely to enhance the initial tendency to void nucleation and growth.

Although the basic and only physical property of the model, namely, $\epsilon(\omega)$, is completely isotropic, the plasmon interaction between the voids is nevertheless capable of inducing "crystallization" of voids into a specific structure, namely, the one whose plasmon band structure will minimize the zero-point energy: Relative stability between different lattice structures can already be discussed in this continuum theory.

What appears to require the anisotropy of the host lattice is the observed fact[2] that the void array has the same structure as the atomic lattice. Void faceting,[10] anisotropic strain fields,[10] anisotropic surface energies of plasmon or other origin, etc., may all contribute to such configuration.

Finally, one would like to suggest that confirmation or contradiction of the present ideas concerning the voids interaction mechanism could be experimentally possible by performing an energy analysis of a fast-electron beam transmitted through the specimen, or by using the technique of energy filtering[16,22] the electron-microscope image of the voids. On increasing the swelling fraction,

the energy loss at $\hbar\omega_p$ due to excitation of the void breathing mode should gradually broaden as a result of the smearing out of the breathing-mode density of states. Such broadening could be observable for aluminum, where the unperturbed plasmon energy is fairly sharp. Unfortunately, the plasmon structure of bulk transition metals where the void arrays have been produced is already so ill defined that it might be difficult to detect even the few-eV broadening of the spectrum, which would correspond to the bandwidth of the breathing mode.

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Optical Properties of Single-Crystal Be from 0.12 to 4.5 eV

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Measurements of the optical absorptivity of single crystals of Be have been carried out in the energy range 0.12–4.5 eV with polarized light. The infrared absorptivity is considerably lower than previously reported. Evidence is presented for the onset of interband transitions for both polarizations beginning near 0.4 eV. A shoulder is noted in the absorptivity for E⊥c at about 1.3 eV. The absorptivity data are Kramers–Kronig analyzed and the optical constants are determined. An interpretation based on the band structure of Tripp, Everett, Gordon, and Stark is presented.

INTRODUCTION

The optical properties of beryllium have been the subject of a number of experimental studies.[1–9] Early workers studied Be films but either performed the evaporation in poor vacua or exposed the samples to contaminating atmospheres before or during the measurements. Tungsten contamina-

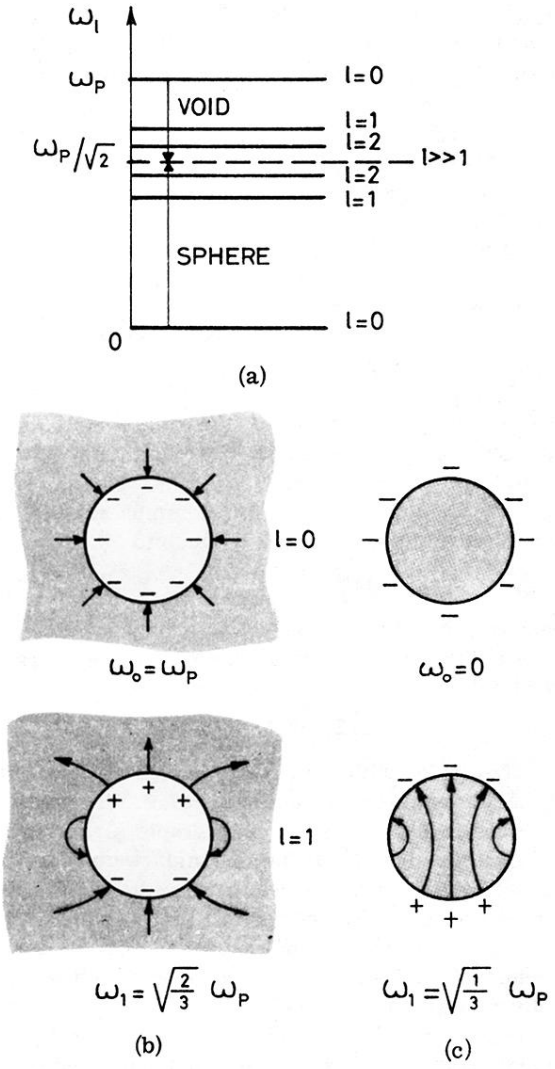

FIG. 1. (a) Spectrum of possible surface-plasmon quanta of a spherical metallic particle (lower half) and of a spherical void in a metal (upper half). The levels l are $2l+1$ degenerate. For large l, both sets converge to the common limit $\omega_p/\sqrt{2}$. The void spectrum is "peeled off" the bulk branch ω_p, whereas the sphere spectrum is "lifted out" of the zero-frequency shear branch $\omega=0$. (b) Mode patterns of electron currents around a void corresponding to the breathing ($l=0$) and dipole ($l=1$) modes. The electron density remains uniform everywhere except on the surfaces, where charges accumulate as shown. (c) Same as in (b), for a full sphere. The zero-frequency $l=0$ surface mode cannot exist without an external singular source or a sink of electrons at the sphere center.