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PHYSICAL REVIEW B VOLUME 7, NUMBER 7 1 APRIL 1973

Plasmons and Characteristic Energy Loss in Periodic Solids

Wayne M. Saslow
Department of Physics, Texas A & M University, College Station, Texas 77843

George F. Reiter
Department of Physics, The City College of the City University of New York, New York, New York 10031

(Received 5 September 1972)

Existing formulations for systems with complete translational invariance relate the dielectric function to the scattering probability in characteristic-energy-loss experiments. We have extended this relationship to the case of periodic systems. Energy-loss vs momentum-transfer measurements are of value because they provide a probe of the system for momentum transfer not accessible to optical measurements. Periodicity is shown to cause the formation of plasmon bands, and the possibility of long-lived higher-band plasmons is discussed. It is concluded that materials with a strong crystalline potential are the best candidates for such higher-band plasmons. The effect of the crystalline potential on the dispersion and damping of the lowest plasmon band, whose existence is well established experimentally, can also be obtained from the formulas that have been derived (which include the effects of local field).

I. INTRODUCTION

At the time when characteristic-energy-loss experiments on thin films were first being performed,[1] the theoretical apparatus for their interpretation was just being developed. Results applicable to the free-electron gas and its collective excitations, the plasmons, were modified in order to explain (in a qualitative fashion) the experiments which were being performed on real solids.[2] These modifications proved highly successful, so much so, that workers in the area were not forced to make more detailed studies. However, had such detailed studies been necessary, they would have been severely handicapped by two major difficulties. First, in most of the early experiments one could not be sure that the thin film was a single crystal, rather than polycrystalline or amorphous. Second, the calculation of properties of periodic solids hinged upon accurate band-structure calculations, which were still in an early stage of development.

Since that time, both experiment and theory have developed considerably. Experiments on thicker films have yielded cartographs of energy loss versus scattering angle which clearly show peaks associated with diffraction by the periodic lattice.[3] In addition, theoretical energy-band calculations have been able to explain numerous properties of periodic solids. However, to our knowledge, no theoretical work has been directed towards explaining the details of the characteristic-energy-loss experiments, including the effects of periodicity on the local field.

We believe it is now appropriate to make such detailed theoretical studies of the energy-loss experiments. Neutron-scattering experiments have revealed much about the vibrations of ions in periodic solids; the analogous electron-scattering experiments should reveal much about the electron energy levels and wave functions in periodic solids. Such studies should provide more detailed information than, e.g., optical studies. We mention that the first detailed calculation of the wave-vector–

dependent dielectric function of a periodic solid has recently been performed,[4] so it should be feasible to perform the electron-energy-loss calculations as well.

It should be pointed out that, in practice, multiple inelastic scattering cannot be ignored.[5] However, the derivation we will give neglects such processes, as well as multiple elastic scattering, and elastic-inelastic-scattering combination processes.

Since plasmon creation dominates the broad features of electron-energy-loss experiments, it is important to study the behavior of plasmons in periodic solids. We find that the eigenvalue equation for plasmons in periodic solids is that $\det\epsilon_{G,G'}(\vec{q},\omega)=0$, where $\epsilon_{G,G'}(\vec{q},\omega)$ may be calculated within the random-phase approximation (RPA) by the prescription of Adler[6] and Wiser.[7] Both the frequency and the damping rate of plasmons are affected by the presence of the periodic potential. For small-momentum plasmons in the lowest plasmon band, the dispersion in the frequency and the plasmon damping will reflect details of the electron band structure. In addition, if distortion of the electron energy levels by the crystalline potential is great enough, some high-momentum plasmons may be long lived. Specifically, since plasmon decay by particle-hole excitation is dependent upon the electronic band structure, a material whose electronic band structure deviates strongly from the free-electron model might support high-momentum plasmons with only a relatively weak damping.

Section II discusses the eigenvalue problem for plasmons in periodic solids. In Secs. III and IV we discuss the energy loss of a charged particle through such a solid. The difference in treatment of a periodic solid and the free-electron gas may be seen by comparing Eqs. (3.15) and (3.16). Section V discusses sum rules and Sec. VI contains a brief summary.

II. PLASMONS IN PERIODIC SOLIDS

A plasmon is a self-sustained charge oscillation: An oscillating electric potential is set up without the introduction of an external charge density. This fact will be used to obtain the condition which determines the plasmon frequencies.

Since the plasmon is a longitudinal mode, it is convenient to consider the response of a periodic solid to an externally applied potential which is purely longitudinal. We set the vector potential $\vec{A}=\vec{0}$, and take (with $\vec{q}$ inside the first Brillouin zone) the total potential $\phi(\vec{r},t)$ to be given by

$$\phi(\vec{r},t)=\frac{1}{(2\pi)^4}\int_{BZ}d^3q\sum_G\int d\omega\, e^{i(\vec{q}+\vec{G})\cdot\vec{r}-i\omega t}\,\phi_G(\vec{q},\omega)\,. \tag{2.1}$$

From the work of Adler and Wiser, it is clear that one may express the Fourier components of $\phi(\vec{r},t)$ in terms of those for the external potential $\phi^{\text{ext}}(\vec{r},t)$:

$$\phi_G(\vec{q},\omega)=\sum_{G'}\epsilon^{-1}_{G,G'}(\vec{q},\omega)\,\phi^{\text{ext}}_{G'}(\vec{q},\omega)\,. \tag{2.2}$$

Here $\epsilon^{-1}_{G,G'}(\vec{q},\omega)$ is the inverse matrix of the dielectric matrix $\epsilon_{G,G'}(\vec{q},\omega)$. This may be inverted to give

$$\phi^{\text{ext}}_G(\vec{q},\omega)=\sum_{G'}\epsilon_{G,G'}(\vec{q},\omega)\,\phi_{G'}(\vec{q},\omega)\,. \tag{2.3}$$

If there is no oscillating externally introduced charge density, then $\phi^{\text{ext}}_G(\vec{q},\omega)=0$ for all $\vec{G}$. This can occur for nonzero $\phi_{G'}(\vec{q},\omega)$ only if

$$\det\epsilon_{G,G'}(\vec{q},\omega)=0\,. \tag{2.4}$$

For a fixed value of $\vec{q}$, this determines the eigenvalues ω. Here the reciprocal-lattice vectors $\vec{G}$ and $\vec{G}'$ serve as indices in the determinant of the dielectric matrix.

To be specific, we present Adler and Wiser's expression for $\epsilon_{G,G'}(\vec{q},\omega)$, which is[6,7]

$$\epsilon_{G,G'}(\vec{q},\omega)=\delta_{G,G'}-G_{G,G'}(\vec{q},\omega)\,|\vec{q}+\vec{G}|^{-2}\,, \tag{2.5}$$

where

$$G_{G,G'}(\vec{q},\omega)=\frac{4\pi e^2}{V}\sum_{\substack{ll'\\ \vec{k}}}\{(l\vec{k}|e^{-i\vec{G}\cdot\vec{r}}|l'\vec{k}+\vec{q})(l'\vec{k}+\vec{q}|e^{i\vec{G}'\cdot\vec{r}}|l\vec{k})[f_0(E_{l\vec{k}})-f_0(E_{l'\vec{k}+\vec{q}})]\}/(h\omega+E_{l\vec{k}}-E_{l'\vec{k}+\vec{q}})\,. \tag{2.6}$$

Here V is the crystal volume (which we will take to be unity), l and l' are band indices, $\vec{k}$ is summed over the first Brillouin zone, and

$$(l\vec{k}|e^{-\vec{G}\cdot\vec{r}}|l'\vec{k}+\vec{q})=(1/V_a)\int_0 d\vec{r}\,u^*_{l\kappa}(\vec{r})\,e^{-i\vec{G}\cdot\vec{r}}\,u_{l'\vec{k}+\vec{q}}(\vec{r})\,. \tag{2.7}$$

The integral is performed over a unit cell, which has the volume V_a, and $u_{lk}(\vec{r})$ is the periodic part of the wave function

$$\langle\vec{r}|l\vec{k}\rangle=V^{-1/2}u_{l\vec{k}}(\vec{r})\,e^{i\vec{k}\cdot\vec{r}}\,.$$

In Eq. (2.6) f_0 denotes the Fermi function and $E_{l\vec{k}}$ is the energy of the state $|l\vec{k}\rangle$.

By comparison with $\epsilon(\vec{q},\omega)$ as derived by Ehrenreich and Cohen,[8] we see that

$$\epsilon_{0,0}(\vec{q},\omega)=\epsilon(\vec{q},\omega)\,. \tag{2.8}$$

In the usual treatment of plasmons in real solids, one replaces the dielectric function of the free-electron gas by $\epsilon(\vec{q},\omega)$, and then finds the zeroes of $\epsilon(\vec{q},\omega)$. As Eq. (2.4) shows, this is not strictly correct. Physically, Eq. (2.4) arises because the charge density responds at wave vectors $\vec{q}+\vec{G}$, for all $\vec{G}$, to a disturbance with wave vector $\vec{q}$, thereby producing the so-called "local field." The crystalline potential causes the formation of plasmon energy bands, just as it causes the formation of electronic energy bands.

It is instructive to consider Eq. (2.4) in the limit of a weak crystalline potential. In that case the off-diagonal elements of $\epsilon_{G,G'}(\vec{q},\omega)$ may be neglected, so

$$\det\epsilon_{G,G'}(\vec{q},\omega)\approx\epsilon_{0,0}(\vec{q},\omega)\,\epsilon_{G_1,G_1}(\vec{q},\omega)\times\epsilon_{G_2,G_2}(\vec{q},\omega)\ldots=0\;. \tag{2.9}$$

Here the subscripts 1 and 2 refer to a labeling of reciprocal-lattice vectors. Further, $\epsilon_{G,G}(\vec{q},\omega)\approx\epsilon_0(\vec{q}+\vec{G},\omega)$ for a weak crystalline potential, where ϵ_0 here denotes the dielectric function of the interacting electron gas. Therefore, Eq. (2.9) tells us that the plasmon bands are formed, in the weak-crystal-field case, by folding the free-plasmon dispersion curve into the first Brillouin zone. Clearly, as the crystalline potential grows, band gaps form at the center and edges of the Brillouin zone.

Of course, this discussion is academic for the case of the free-electron model, since the plasmons in the higher bands, and even high $\vec{q}$ plasmons in the lowest band, will be strongly damped. As the crystalline potential becomes more important, the damping of the plasmons in the lowest bands will become strongly affected. We note, however, that just as high-lying electronic energy bands are very free-electron-like (since the crystal potential is very weak compared to the kinetic energy of the electron), so high-lying plasmon energy bands are very free-electron-like, and therefore highly damped. This is because the decay of such a high-energy plasmon involves the excitation of an electron into a high-energy electronic state. These states are nearly-free-electron-like, and thus permit a near continuum of particle-hole excitations, thereby damping the high-energy plasmon. Such may not be the case for the lower plasmon bands, for which the decay process involves electronic energy levels which have been strongly affected by the crystalline potential. For materials with strong crystalline potentials, it might be the case that the second lowest-lying plasmon band has long-lived plasmons with $\vec{q}\approx\vec{0}$ (i.e., where there is an optical band gap). To see if this is the case, explicit and detailed calculations are necessary. Strongly covalent and strongly ionic crystals would be good candidates for such calculations.

We remark that it is probably overly optimistic to expect truly long-lived plasmons in higher bands However, it would not be surprising to find diffuse peaks in the energy-loss spectra which can be associated with "incipient" higher-band plasmons. Such peaks would most likely not appear in samples which are not truly crystalline. This dependence upon crystallinity may explain why certain energy-loss peaks are observed by some experimentalists, but not by others.

In the next sections we compute the energy loss of a high-energy charged particle when it travels through a periodic solid, in order to see how these plasmons might show up in an energy-loss experiment.

III. ENERGY LOSS BY A CHARGED PARTICLE

We consider here the energy given to a periodic solid when a high-energy charged particle (an electron) moves through it. Our calculation in this section will be classical: We will compute the rate of work done by a localized particle as it moves through the solid. The particle, of charge $-e$, will be considered to be moving with the constant velocity $\vec{V}_e$ (we neglect momentum loss by the particle), and is localized at $\vec{r}=\vec{0}$ when $t=0$:

$$\rho^{\text{ext}}(\vec{r},t)=-e\delta(\vec{r}-\vec{V}_e t)\;. \tag{3.1}$$

ρ^{ext} denotes the external charge density.

The change in energy when a charge distribution is changed is given by[9]

$$\delta U=\int d\vec{r}\,\phi(\vec{r})\delta\rho(\vec{r})\;. \tag{3.2}$$

Therefore the rate at which this energy is changed is given by

$$\frac{dU}{dt}=\int d\vec{r}\;\phi(\vec{r})\,\frac{\partial\rho(\vec{r})}{\partial t}\;. \tag{3.3}$$

We want only the change arising from the induced charge density, or

$$\frac{dW}{dt}=\int d\vec{r}\,\phi\,\frac{\partial\rho^{\text{ind}}}{\partial t}\;. \tag{3.4}$$

It is most convenient to Fourier analyze ϕ and ρ^{ind}. Use of Poisson's equation will then exhibit the relationship of the Fourier components of ϕ and ρ^{ind} to those of ρ^{ext}. We have

$$\rho_G^{\text{ext}}(\vec{q},\omega)=\int d\vec{r}\,d\omega\,e^{-i(\vec{q}+\vec{G})\cdot\vec{r}+i\omega t}\,\rho^{\text{ext}}(\vec{r},t)=-2\pi e\delta[\omega-\vec{V}_e\cdot(\vec{q}+\vec{G})]\;. \tag{3.5}$$

From Poisson's equation

$$\nabla^2\phi=-4\pi\rho\;, \tag{3.6}$$

one can show that

$$\phi_G^{\text{ext}}(\vec{q},\omega)=4\pi\,|\vec{q}+\vec{G}|^{-2}\rho_G^{\text{ext}}(\vec{q},\omega) \tag{3.7}$$

and

$$\phi_G(\vec{q},\omega)=4\pi\,|\vec{q}+\vec{G}|^{-2}[\rho_G^{\rm ext}(\vec{q},\omega)+\rho_G^{\rm ind}(\vec{q},\omega)]\,. \tag{3.8}$$

Then from Eqs. (2.2) and (3.7) it is seen that

$$\phi_G(\vec{q},\omega)=4\pi\sum_{G'}\epsilon^{-1}_{G,G'}(\vec{q},\omega)\,|\vec{q}+\vec{G}'|^{-2}\rho_{G'}^{\rm ext}(\vec{q},\omega)\,. \tag{3.9}$$

From Eqs. (3.8) and (3.9) one may show that

$$\begin{aligned}\rho_G^{\rm ind}(\vec{q},\omega)&=-\rho_G^{\rm ext}(\vec{q},\omega)+|\vec{q}+\vec{G}|^2\sum_{G'}\epsilon^{-1}_{G,G'}(\vec{q},\omega)\,|\vec{q}+\vec{G}'|^{-2}\rho_{G'}^{\rm ext}(\vec{q},\omega)\\&=\sum_{G'}[-\delta_{G,G'}+|\vec{q}+\vec{G}|^2\epsilon^{-1}_{G,G'}(\vec{q},\omega)\,|\vec{q}+\vec{G}'|^{-2}]\rho_{G'}^{\rm ext}(\vec{q},\omega)\,.\end{aligned} \tag{3.10}$$

Using Eqs. (3.9) and (3.10) and the Fourier representations of ϕ and $\rho^{\rm ind}$, Eq. (3.4) becomes

$$\begin{aligned}\frac{dW}{dt}&=\int d\vec{r}\,\frac{1}{(2\pi)^4}\int_{\rm BZ}d\vec{q}\sum_G\int d\omega\,e^{i(\vec{q}+\vec{G})\cdot\vec{r}-i\omega t}\,\phi_G(\vec{q},\omega)\,\frac{\partial}{\partial t}\,\frac{1}{(2\pi)^4}\int_{\rm BZ}d\vec{q}\,'\sum_{G'}\int d\omega'\,e^{i(\vec{q}\,'+\vec{G}')\cdot\vec{r}-i\omega' t}\,\rho_{G'}^{\rm ind}(\vec{q}\,',\omega')\\&=\frac{-i}{(2\pi)^5}\int_{\rm BZ}d\vec{q}\sum_G\int d\omega\int d\omega'\,e^{-i(\omega+\omega')t}\,\omega'\,\phi_G(\vec{q},\omega)\,\rho_{-G}^{\rm ind}(-\vec{q},\omega')\\&=-\frac{4\pi i}{(2\pi)^5}\int_{\rm BZ}d\vec{q}\sum_{\rm G}\int d\omega\int d\omega'\,e^{-i(\omega+\omega')t}\,\omega'\sum_{G'}\epsilon^{-1}_{G,G'}(\vec{q},\omega)|\vec{q}+\vec{G}'|^{-2}\rho_{G'}^{\rm ext}(\vec{q},\omega)\\&\qquad\times\sum_{G''}[-\delta_{-G,G''}+|\vec{q}+\vec{G}|^2\epsilon^{-1}_{-G,G''}(-\vec{q},\omega')\,|\vec{q}-\vec{G}''|^{-2}]\rho_{G''}^{\rm ext}(-\vec{q},\omega')\,.\end{aligned} \tag{3.11}$$

Use of Eq. (3.5) simplifies Eq. (3.11) to

$$\begin{aligned}\frac{dW}{dt}=-\frac{e^2 i}{2\pi^2}\int_{\rm BZ}d\vec{q}\sum_{GG'G''}e^{-i\vec{V}_e\cdot(\vec{G}'+\vec{G}'')t}\,[\epsilon^{-1}_{G,G'}(\vec{q},\vec{V}_e\cdot(\vec{q}+\vec{G}'))\vec{V}_e\cdot(-\vec{q}+\vec{G}'')]\\\times[-|\vec{q}+\vec{G}'|^{-2}\delta_{-G,G''}+\epsilon^{-1}_{-G,G''}(-\vec{q},\vec{V}_e\cdot(-\vec{q}+\vec{G}''))\,|\vec{q}-\vec{G}''|^{-2}\,|\vec{q}+\vec{G}'|^{-2}\,|\vec{q}+\vec{G}|^2]\,.\end{aligned} \tag{3.12}$$

The time average of dW/dt is nonzero only when $\vec{G}''=-\vec{G}'$, so

$$\begin{aligned}\left\langle\frac{dW}{dt}\right\rangle=\frac{e^2 i}{2\pi^2}\int_{\rm BZ}d\vec{q}\sum_{GG'}\epsilon^{-1}_{G,G'}(\vec{q},\vec{V}_e\cdot(\vec{q}+\vec{G}'))\vec{V}_e\cdot(\vec{q}+\vec{G}')[-|\vec{q}+\vec{G}|^2\delta_{G,G'}\\+\epsilon^{-1}_{-G,-G'}(-\vec{q},-\vec{V}_e\cdot(\vec{q}+\vec{G}'))\,|\vec{q}+\vec{G}|^2\,|\vec{q}+\vec{G}'|^{-4}]\,.\end{aligned} \tag{3.13}$$

Since only the real part of $\langle dW/dt\rangle$ matters, only the imaginary part of the term proportional to $\delta_{G,G'}$ is kept. This is because

$$\epsilon^{-1}_{G,G'}(\vec{q},\omega)=[\epsilon^{-1}_{-G,-G'}(-\vec{q},-\omega)]^*\,, \tag{3.14}$$

as is shown in Appendix A. Finally,

$$P\equiv{\rm Re}\left\langle\frac{dW}{dt}\right\rangle=\frac{e^2}{2\pi^2}\int_{\rm BZ}d\vec{q}\sum_G\frac{\vec{V}_e\cdot(\vec{q}+\vec{G})}{|\vec{q}+\vec{G}|^2}\times{\rm Im}[-\epsilon^{-1}_{G,G}(\vec{q},\vec{V}_e\cdot(\vec{q}+\vec{G}))]\,. \tag{3.15}$$

In the absence of a crystalline potential, this expression reduces to the standard result for a translationally invariant system:

$$P=\frac{e^2}{2\pi^2}\int d\vec{q}\,\frac{\vec{V}_e\cdot\vec{q}}{|\vec{q}|^2}\,{\rm Im}\left(-\frac{1}{\epsilon(\vec{q},\vec{V}_e\cdot\vec{q})}\right)\,. \tag{3.16}$$

In Eq. (3.16) the integral is taken over all $\vec{q}$, not merely over the first Brillouin zone as in Eq. (3.15).

In Eq. (3.15), ${\rm Im}[\epsilon^{-1}_{G,G}(\vec{q},\vec{V}_e\cdot(\vec{q}+\vec{G}))]$ takes on large values in the vicinity of the frequency of plasmons. If the plasmons are weakly damped, this peak will be quite large, which implies that the fast charged particle is effective in creating these plasmons. It is possible that some of the peaks seen in characteristic-energy-ions experiments are due to the generation of higher-band plasmons, since the detailed form of these energy-loss spectra are not well understood. Application of Eq. (2.4) and (3.15) requires a detailed knowledge of the electronic band structure. We have not yet applied the formalism to any specific materials.

It should be remarked that Walter and Cohen[4] have studied (for Si, and within the RPA) plasmon energies for the lowest band, with the neglect of the off-diagonal terms in Eq. (2.4). They have also studied $\mathrm{Im}\{-[\epsilon_{00}(\vec{q},\omega)]^{-1}\}$ for Si. Their work will be discussed later. As has just been shown, the off-diagonal terms in the dielectric matrix (i.e., the local field) must be included in an exact calculation of the plasmon energy and the characteristic energy loss. The effects of including these terms are not immediately obvious, and they will most likely not become clear until detailed numerical calculations have been performed.

IV. ANGULAR DISTRIBUTION OF ELECTRON ENERGY LOSS

In this section we discuss how one may determine the angular distribution of electron energy loss. Our arguments follow closely the work of Pines and Nozières.[10] They show that the probability per unit time $P(\vec{q}+\vec{G},\omega)$ that the electron transfer momentum $\vec{q}+\vec{G}$ and energy ω to the system ($\hbar=1$) is given by

$$P(\vec{q}+\vec{G},\omega)=2\pi\,|V_{\vec{q}+\vec{G}}|^2\sum_n|\langle n|\rho_{-G}^{\mathrm{ind}}(-\vec{q})|0\rangle|^2\times\delta(\omega-\omega_{no})\,. \quad (4.1)$$

Here $V_{\vec{q}+\vec{G}}=-4\pi e/|\vec{q}+\vec{G}|^2$ is the spatial Fourier transform of the potential of the incoming electron, $\rho_G^{\mathrm{ind}}(\vec{q})=-e\sum_i e^{-i(\vec{q}+\vec{G})\cdot\vec{r}_i}$ is summed over all particle coordinates $\vec{r}_i$, and the sum on n is performed over the exact states $|n\rangle$ of the system, with the exception of the ground state, denoted by $|0\rangle$. Also, $\omega_{no}=\omega_n-\omega_o$ is the energy difference between the states $|n\rangle$ and $|0\rangle$. We note that our $\rho\to -e$ times the ρ of Ref. 10, and our $V\to -e^{-1}$ times the V of Ref. 10.

Equation (4.1) was derived under the assumption of single scattering, so it is not applicable to multiple plasmon excitation, which has been observed even for films as thin as 200 Å.[11] In addition, no assumption of crystallinity was made, so our further results will be applicable to crystals of any symmetry. Equation (4.1) is conveniently separated into two parts:

$$P(\vec{q}+\vec{G},\omega)=2\pi\,|V_{\vec{q}+\vec{G}}|^2e^2S(\vec{q}+\vec{G},\omega)\,, \quad (4.2)$$

where

$$S(\vec{q}+\vec{G},\omega)=e^{-2}\sum_n|\langle n|\rho_{-G}^{\mathrm{ind}}(-\vec{q})|0\rangle|^2\delta(\omega-\omega_{n0}) \quad (4.3)$$

is known as the dynamic form factor of the system. Our purpose is to relate $S(\vec{q}+\vec{G},\omega)$ to $\epsilon_{G,G}^{-1}(\vec{q},\omega)$, thereby demonstrating that $P(\vec{q}+\vec{G},\omega)$ may be expressed in terms of the inverse dielectric function. The main results of Sec. III may be derived using $P(\vec{q}+\vec{G},\omega)$.

We now display an expression for $\epsilon_{G,G'}^{-1}(\vec{q})$ in terms of the exact states of the system. From Eq. (2.4),

$$\epsilon_{G,G'}^{-1}(\vec{q},\omega)=\frac{\delta\phi_G(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}\,. \quad (4.4)$$

Now

$$\delta\phi_G(\vec{q},\omega)=\delta\,\phi_G^{\mathrm{ext}}(\vec{q},\omega)+\delta\phi_G^{\mathrm{ind}}(\vec{q},\omega)\,, \quad (4.5)$$

so

$$\epsilon_{G,G'}^{-1}(\vec{q},\omega)=\delta_{G,G'}+\frac{\delta\phi_G^{\mathrm{ind}}(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}\,, \quad (4.6)$$

since

$$\frac{\delta\phi_G^{\mathrm{ext}}(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}=\delta_{G,G'}\,.$$

Further, from Poisson's equation,

$$\delta\phi_G^{\mathrm{ind}}(\vec{q},\omega)=4\pi|\vec{q}+\vec{G}|^{-2}\delta\rho_G^{\mathrm{ind}}(\vec{q},\omega)\,, \quad (4.7)$$

so

$$\epsilon_{G,G'}^{-1}(\vec{q},\omega)=\delta_{G,G'}+4\pi|\vec{q}+\vec{G}|^{-2}\,\frac{\delta\rho_G^{\mathrm{ind}}(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}\,. \quad (4.8)$$

This equation has been derived by Martin and Schwinger.[12] We may calculate $\delta\rho_G^{\mathrm{ind}}(\vec{q},\omega)/\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)$ using linear-response theory. It should be noted that only the diagonal elements of ϵ^{-1} will be needed, so that the calculation of Ref. 10, for a translationally invariant system, may be carried over. Denoting

$$\chi_{G,G'}(\vec{q},\omega)=\frac{\delta\rho_G^{\mathrm{ind}}(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}\,, \quad (4.9)$$

then from Ref. 10,

$$\chi_{G,G}(\vec{q},\omega)=\sum_n|\langle n|\rho_{-G}^{\mathrm{ind}}(-\vec{q})|0\rangle|^2\,2\omega_{n0}\times[(\omega+i\eta)^2-\omega_{n0}^2]^{-1}. \quad (4.10)$$

Here η is a positive infinitesimal which has been introduced so that $\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)$ may be considered to have been turned on adiabatically. $\chi_{G,G'}(\vec{q},\omega)$ for $G\neq G'$ is calculated in Appendix B. From Eqs. (4.8)–(4.10) it is clear that

$$\epsilon_{G,G}^{-1}(\vec{q},\omega)=1+4\pi|\vec{q}+\vec{G}|^{-2}\sum_n|\langle n|\rho_{-G}^{\mathrm{ind}}(-\vec{q})|0\rangle|^2\times\left(\frac{1}{\omega-\omega_{n0}+i\eta}-\frac{1}{\omega+\omega_{n0}+i\eta}\right). \quad (4.11)$$

Then

$$\mathrm{Im}\,\epsilon_{G,G}^{-1}(\vec{q},\omega)=-4\pi^2e^2|\vec{q}+\vec{G}|^{-2}[S(\vec{q}+\vec{G},\omega)-S(\vec{q}+\vec{G},-\omega)]. \quad (4.12)$$

For $\omega>0$ this gives, on comparison with Eq. (4.3),

$$S(\vec{q}+\vec{G},\omega)=-\frac{|\vec{q}+\vec{G}|^2}{4\pi^2e^2}\,\mathrm{Im}\,\epsilon_{G,G}^{-1}(\vec{q},\omega), \quad (4.13)$$

so

$$P(\vec{q}+\vec{G},\omega)=\frac{8\pi e^2}{|\vec{q}+\vec{G}|^2}\left[-\operatorname{Im}\epsilon^{-1}_{G,G}(\vec{q},\omega)\right] \quad . \tag{4.14}$$

The rate of energy loss to the medium due to all excitations is given by

$$\begin{aligned}P&=\sum_q\sum_G \omega P(\vec{q},\omega)\\ &=\frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} d^3q\sum_G \omega\, P(\vec{q}+\vec{G},\omega) \ ,\end{aligned} \tag{4.15}$$

where $\omega=\vec{V}_e\cdot(\vec{q}+\vec{G})$. This equation is identical to Eq. (3.15), derived from classical considerations.

The equations describing energy loss for a system with complete translational invariance go over smoothly to the corresponding equations for a periodic system. Therefore $P(\Omega,\omega)d\Omega$, the probability per unit time that the electron will be scattered into a solid angle $d\Omega=2\pi\sin\Theta\, d\Theta$, while suffering an energy loss ω, can be obtained by only slight modification of the expression given in Ref. 10. For momentum transfer which is small compared to P_e, the momentum of the incoming electron, $P(\Omega,\omega)$ is given by[10]

$$P(\Omega,\omega)=\left[P_e^2/(2\pi)^3\right]\int dq'_{\parallel}P(\vec{q},\omega)\,\delta(\omega-q'_{\parallel}v_e) \quad . \tag{4.16}$$

Here $\vec{q}\,'$ is not restricted to the first Brillouin zone, and $q'_{\parallel}v_e=\vec{q}\,'\cdot\vec{v}_e$. $P(\vec{q}\,',\omega)$ is calculated using Eq. (4.14) and $\vec{q}\,'=\vec{q}+\vec{G}$.

With Eqs. (4.14) and (4.16) one can compare theory to experiment. The availability of detailed cartographs of energy loss versus momentum, providing a probe of the solid for appreciable momentum transfer, should ultimately permit a more exhaustive test of our knowledge of energy bands in solids than optical-absorption data have permitted. (This situation, of course, arises because the wave vector can be varied in electron-scattering measurements, whereas it must be near the value zero for optical-absorption measurements.) To our knowledge, no one has yet attempted to calculate such cartographs.

In addition to studying the details of the band structure by comparison with data for the lowest plasmon band, such calculations can indicate the presence (or absence) of higher-band plasmons.

V. SUM RULES FOR PERIODIC SYSTEM

A number of sum rules which apply to a system with complete translational invariance also apply, with suitable modification, to a periodic system. We will discuss two of them because the presence of plasmons affects the weighting within these sum rules, causing this collective effect to outweigh the individual particle contributions.

The f sum rule will be used in conjunction with Eq. (4.11) to obtain the high-frequency behavior of the dielectric function. Since it is derived for the exact states of an arbitrary system, it is also applicable to periodic systems. Specifically,[10]

$$\sum_n \omega_{n0}\left|\langle n|\rho_G^\dagger(\vec{q})|0\rangle\right|^2=N(\vec{q}+\vec{G})^2/2m \quad . \tag{5.1}$$

We have dropped the superscript "ind" on the quantity $\rho_G^\dagger(\vec{q})$. Considering Eq. (4.11) in the high-frequency limit, use of Eq. (5.1) enables us to obtain the relation [accurate to $0(\omega^{-2})$]

$$\epsilon^{-1}_{G,G}(\vec{q},\omega)\xrightarrow[\omega\to\infty]{}1+\omega_p^2/\omega^2, \tag{5.2}$$

where

$$\omega_p^2=4\pi Ne^2/m \quad . \tag{5.3}$$

(The volume $V=1$, so the number density n equals the number of electrons N which are not in the core states. By $\omega\to\infty$ we mean $\omega\gg$ valence to conduction-band energies.) In the high-frequency limit the effect of the off-diagonal elements of $\epsilon^{-1}_{G,G'}(\vec{q},\omega)$ can be neglected, so $\epsilon^{-1}_{G,G'}(\vec{q},\omega)$ may be inverted simply to give, to $O(\omega^{-2})$,

$$\epsilon_{G,G}(\vec{q},\omega)\xrightarrow[\omega\to\infty]{}1-\omega_p^2/\omega^2 \ , \quad . \tag{5.4}$$

Using Eqs. (5.2) and (5.4) and the Kramers–Kronig relations, the proofs given in Ref. 10 carry over completely, so that we obtain the two sum rules

$$\int_0^\infty d\omega\,\omega\,\operatorname{Im}\left[\epsilon^{-1}_{G,G}(\vec{q},\omega)\right]=-\tfrac{1}{2}\pi\,\omega_p^2 \ , \tag{5.5}$$

$$\int_0^\infty d\omega\,\omega\,\operatorname{Im}\left[\epsilon_{G,G}(\vec{q},\omega)\right]=\tfrac{1}{2}\pi\,\omega_p^2 \ . \tag{5.6}$$

The first of these is a restatement of the f sum rule. The second is called the "conductivity" sum rule.[10] It is clear that the presence of a plasmon will cause these sum rules to have a large contribution from the region in which the plasmon is well defined; conversely, the presence of a plasmon causes the single-particle or multiparticle excitations to give a weaker contribution to the sum rules.

VI. DISCUSSION

We have studied the question of characteristic energy loss by a periodic solid, including the effects of the local fields and of the detailed band structure of the solid. The effect of periodicity on bulk plasmons has been discussed. It has been suggested that, in materials with a strong crystalline potential, plasmons in higher bands may be long-lived enough to be observed in energy-loss experiments.

We note that even in the absence of higher-band plasmons, the effects of periodicity on the lowest plasmon band cannot be neglected.

(i) Plasmon dispersion depends upon the detailed structure of the electronic energy bands. This can be seen from the calculations of Ref. 4 on Si, which [although they are based upon an RPA $\epsilon_{00}(\vec{q}, \omega)$ rather than the full dielectric matrix] demonstrate the order of magnitude of such effects. In particular, the dispersion of the lowest plasmon band is found to be approximately two-thirds the value one would predict on the basis of the RPA for the free-electron model (see Fig. 13 of Ref. 4).

(ii) Plasmon damping depends upon the detailed structure of the electronic energy bands, as can also be seen from the calculations of Ref. 4 for Si. Even for $\vec{q}=\vec{0}$ and within the RPA, the plasmon from the lowest band has a finite damping. This is expected to remain even in calculations using the full dielectric matrix. In this regard, DuBois and Kivelson[13] have recently performed a calculation of plasmon damping for the free-electron gas, including some electron correlation effects which are not included in the RPA. They were interested in making comparison with experiments on Al,[14-16] a material whose band structure is much more free-electron-like than that of Si, The theoretical damping was found to be considerably less than that obtained experimentally. Of the possible additional causes of damping (in addition to correlation effects not included in Ref. 13, and in addition to scattering by impurities and by phonons), the effects of the periodic lattice can be determined from Eq. (2.4). We remark that Foo and Hopfield[17] have studied a simple model, with one reciprocal-lattice vector, for the dielectric function of sodium. They found the interesting result that for a narrow range of momentum transfer $\vec{q}$, the presence of the band gap (and the large density of states associated with it) caused a large peak in the energy loss plotted as a function of ω. This phenomenon can also be expected to occur in calculations on more complex systems. It is not associated with higher-band plasmons.

ACKNOWLEDGMENTS

We would like to acknowledge conversations with M. L. Cohen, R. M. Martin, and J. W. Wilkins, and conversations and correspondence with L. Marton.

APPENDIX A

We wish to establish the relationship

$$\epsilon^{-1}_{G,G'}(\vec{q}, \omega) = [\epsilon^{-1}_{-G,-G'}(-\vec{q}, -\omega)]^*. \tag{A1}$$

This is obtained by considering an external potential which is real:

$$\phi^{\text{ext}}(\vec{r}, t) = e^{i(\vec{q}+\vec{G})\cdot r - i\omega t} + e^{-i(\vec{q}+\vec{G})\cdot r + i\omega t} \quad . \tag{A2}$$

This corresponds to

$$\phi^{\text{ext}}_{G'}(\vec{q}', \omega') = (2\pi)^4 [\delta(\vec{q}-\vec{q}')\,\delta(\omega-\omega')\,\delta_{G,G'} + \delta(\vec{q}+q')\,\delta(\omega+\omega')\,\delta_{G,-G'}] \quad . \tag{A3}$$

From Eqs. (2.1) and (2.2) this gives

$$\phi(\vec{r}, t) = \sum_{G''} [\epsilon^{-1}_{G'',G}(\vec{q}, \omega)\, e^{i(\vec{q}+\vec{G}'')\cdot\vec{r} - i\omega t} + \epsilon^{-1}_{-G'',-G}(-\vec{q}, -\omega)\, e^{-i(\vec{q}+\vec{G}'')\cdot\vec{r} + i\omega t}] \quad . \tag{A4}$$

Since $\phi^{\text{ext}}(\vec{r}, t)$ is real, so must $\phi(\vec{r}, t)$ be real, from which one may deduce Eq. (A1). One may similarly deduce that

$$\epsilon_{G,G'}(\vec{q}, \omega) = [\epsilon_{-G,-G'}(-\vec{q}, -\omega)]^* \quad . \tag{A5}$$

APPENDIX B

In this Appendix we derive an expression for $\chi_{G,G'}(\vec{q}, \omega)$. This will be done by the use of linear-response theory, as outlined in Ref. 10.

We must begin with the Hamiltonian describing the interaction between the solid and incoming electron. This is given by

$$H_{\text{int}} = \sum_i V(\vec{r}_i - \vec{R}_e) \quad , \tag{B1}$$

where

$$V(\vec{r}_i - \vec{R}_e) = e^2/|\vec{r}_i - \vec{R}_e| \quad . \tag{B2}$$

Here $\vec{R}_e = \vec{V}_e t$ is the position of the incoming electron, and the $\vec{r}_i$ are the positions of the electrons in the solid. Equation (B1) may be rewritten

$$H_{\text{int}} = \sum_i \sum_{q\in\text{BZ}} \sum_G e^{i(\vec{q}+\vec{G})\cdot(\vec{r}_i - \vec{R}e)}(-e)V_G(\vec{q}), \tag{B3}$$

where

$$V_G(\vec{q}) = \int d^3r\,[(-e)/r]\,e^{-i(\vec{q}+\vec{G})\cdot\vec{r}} = -4\pi e/(|\vec{q}+\vec{G}|^2) \quad . \tag{B4}$$

Then

$$H_{\text{int}} = \sum_{q\in\text{BZ}} \sum_G \rho^{\text{ind}}_{-G}(-\vec{q})\, V_G(\vec{q})\, e^{-i(\vec{q}+\vec{G})\cdot\vec{R}_e} \quad , \tag{B5}$$

where

$$\rho^{\text{ind}}_G(\vec{q}) = -e\sum_i e^{-i(\vec{q}+\vec{G})\vec{r}_i} \quad . \tag{B6}$$

This can also be written

$$H_{\text{int}} = \sum_{q\in\text{BZ}} \sum_{G} \int \frac{d\omega}{2\pi}\, \rho^{\text{ind}}_{-G}(-\vec{q})\, \phi^{\text{ext}}_G(\vec{q}, \omega)\, e^{-i\omega t} , \tag{B7}$$

with

$$\phi^{\text{ext}}_G(\vec{q}, \omega) = 2\pi\, V_G(\vec{q})\, \delta[\omega - (\vec{q}+\vec{G})\cdot\vec{V}_e] \quad . \tag{B8}$$

We note that Eq. (B8) is consistent with Eqs. (3.7) and (3.5). Because the interaction is a real number, we must have

$$\phi^{\text{ext}}_G(\vec{q}, \omega) = [\phi^{\text{ext}}_{-G}(-\vec{q}, -\omega)]^* , \tag{B9}$$

which may be verified directly using Eq. (B8).

We wish to determine

$$\chi_{G,G'}(\vec{q},\omega)=\frac{\delta\rho_G^{\mathrm{ind}}(\vec{q},\omega)}{\delta\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}\ . \tag{B10}$$

To do this we will consider $\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)$ as a perturbation in Eq. (B7) and find the response to it.

We wish to compute

$$\rho_G^{\mathrm{ind}}(\vec{q},\omega)=\int dt\, e^{i\omega t}\rho_G^{\mathrm{ind}}(\vec{q},t)\ , \tag{B11}$$

where

$$\rho_G^{\mathrm{ind}}(\vec{q},t)=\langle\psi(\vec{r},t)\,|\rho_G^{\mathrm{ind}}(\vec{q})|\,\psi(\vec{r},t)\rangle\ . \tag{B12}$$

As the interaction it will be sufficient to consider

$$H'=(e^{\eta t}/2\pi)[\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)e^{-i\omega t}+\mathrm{c.\,c.}]\ , \tag{B13}$$

where η is a positive infinitesimal which guarantees that the interaction is turned on adiabatically.

Using

$$i\frac{d}{dt}\,|\psi(t)\rangle=(H+H')\,|\psi(t)\rangle\ , \tag{B14}$$

where H, the Hamiltonian of the solid, satisfies

$$H\,|n\rangle=E_n\,|n\rangle\ , \tag{B15}$$

$|\psi(t)\rangle$ is expanded in terms of the eigenstates $|n\rangle$:

$$|\psi(t)\rangle=\sum_n a_n(t)e^{-iE_nt}\,|n\rangle\ . \tag{B16}$$

With the boundary condition

$$a_n(-\infty)=\begin{matrix}1\ , & n=0\\ 0\ , & n\neq 0\ ,\end{matrix} \tag{B17}$$

corresponding to the system being in its ground state at $t=-\infty$, one may easily show that

$$a_n(t)=\frac{e^{\eta t}}{2\pi}\left(\frac{\langle n\,|\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\,|0\rangle\ \phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}{\omega-\omega_{n0}+i\eta}\,e^{i(\omega_{n0}-\omega)t}-\frac{\langle n\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|0\rangle\ \phi_{-G'}^{\mathrm{ext}}(-\vec{q},-\omega)}{\omega+\omega_{n0}-i\eta}\,e^{i(\omega_{n0}+\omega)t}\right)\ . \tag{B18}$$

Then

$$\begin{aligned}\rho_G^{\mathrm{ind}}(\vec{q},t)&=\sum_n\Big(\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|\,n\rangle\ a_n(t)e^{-i\omega_{n0}t}+\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\ a_n^*(t)e^{i\omega_{n0}t}\Big)\\&=\frac{e^{\eta t}}{2\pi}\sum_n\left(\frac{\langle 0\,|\,\rho_G^{\mathrm{ind}}(\vec{q})\,|n\rangle\langle n\,|\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\,|0\rangle\ \phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)}{\omega-\omega_{n0}+i\eta}\,e^{-i\omega t}-\frac{\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|n\rangle\langle n\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|0\rangle\ \phi_{-G'}^{\mathrm{ext}}(-\vec{q},\omega)}{\omega+\omega_{n0}-i\eta}\,e^{i\omega t}\right.\\&\quad\left.+\frac{\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\langle n\,|\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\,|0\rangle^*\ \phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)^*}{\omega-\omega_{n0}-i\eta}\,e^{i\omega t}-\frac{\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\langle n\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|0\rangle^*\ \phi_{-G'}^{\mathrm{ext}}(-\vec{q},-\omega)^*}{\omega+\omega_{n0}+i\eta}\,e^{-i\omega t}\right)\ .\end{aligned} \tag{B19}$$

Note that $|n\rangle$ is an eigenstate of momentum (modulo a reciprocal-lattice vector). Therefore, for $\vec{q}$ not on the Brillouin-zone face, $\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\neq 0$ implies that $\langle n\,|\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\,|\,0\rangle=0$, and vice versa. Hence the second and third terms in the large parentheses of Eq. (B19) are zero. Use of Eq. (B9) and the relation

$$\langle n\,|\rho_{-G'}^{\mathrm{ind}}(-\vec{q})\,|0\rangle=\langle 0\,|\,\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|n\rangle^* \tag{B20}$$

permits Eq. (B19) to be written

$$\rho_G^{\mathrm{ind}}(\vec{q},t)=\frac{e^{(i\omega+\eta)t}}{2\pi}\,\phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)\sum_n\left(\frac{\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|n\rangle\ \langle 0\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|n\rangle^*}{\omega-\omega_{n0}+i\eta}-\frac{\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\langle n\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|0\rangle^*}{\omega+\omega_{n0}+i\eta}\right)\ . \tag{B21}$$

By time-reversal invariance, for each state $|n\rangle$ with reduced wave vector $\vec{q}$ there is a state $|m\rangle$ with reduced wave vector $-\vec{q}$, having the same energy and a complex conjugate wave function. This permits the replacement of

$$\sum_n\frac{\langle n\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|0\rangle\langle n\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|0\rangle^*}{\omega+\omega_{n0}+i\eta}$$

by

$$\sum_m\frac{\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|m\rangle\langle 0\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|m\rangle^*}{\omega+\omega_{m0}+i\eta}\ ,$$

so Eq. (B21) may be written

$$\rho_G^{\mathrm{ind}}(\vec{q},t)=\frac{e^{(i\omega+\eta)t}}{2\pi}\ \phi_{G'}^{\mathrm{ext}}(\vec{q},\omega)\sum_n\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|n\rangle\times\langle 0\,|\,\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|n\rangle^*\,2\omega_{n0}/[(\omega+i\eta)^2-\omega_{n0}^2]\ . \tag{B22}$$

Then, using $(1/2\pi)\int dt\,e^{i(\omega-\omega')t}=\delta(\omega-\omega')$ and Eq. (B10), we have

$$\chi_{G,G'}(\vec{q},\omega)=\sum_n\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\,|n\rangle\langle 0\,|\rho_{G'}^{\mathrm{ind}}(\vec{q})\,|n\rangle^*\times 2\omega_0/[(\omega+i\eta)^2-\omega_{n0}^2]\ . \tag{B23}$$

Note that $n=0$ is excluded from $\sum_n$, since $\langle 0\,|\rho_G^{\mathrm{ind}}(\vec{q})\times|0\rangle=0$ for $\vec{q}+\vec{G}\neq\vec{0}$. For $\vec{G}=\vec{G}'$, Eq. (B23) is identical to Eq. (4.10) of the text.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 7 1 APRIL 1973

Electron-Paramagnetic-Resonance Investigation of the Dynamic Jahn–Teller Effect in $SrCl_2:Y^{2+}$ and $SrCl_2:Sc^{2+}$

J. R. Herrington*† and T. L. Estle*
Physics Department, Rice University, Houston, Texas 77001

L. A. Boatner
Advanced Technology Center, Inc.,‡ Dallas, Texas 75222

(Received 13 October 1972)

EPR spectra have been observed for $SrCl_2:Y^{2+}$ and $SrCl_2:Sc^{2+}$ at liquid-helium temperatures. At 1.2 K the spectra were dominated by anisotropic hyperfine patterns whose line shapes and angular dependences were explained using second-order solutions of the effective Hamiltonian for an isolated ^2E_g state split by large random internal strains. Pronounced asymmetries in some of the strain-produced line shapes for $SrCl_2:Sc^{2+}$ are shown to result from second-order terms in the solution of the effective Hamiltonian. Coexisting with the anisotropic hyperfine patterns are weak nearly isotropic hyperfine patterns with typical line shapes. Variations in the apparent intensity of lines in these weak hyperfine patterns as functions of the applied-magnetic-field direction and temperature imply that these lines result from averaging by vibronic relaxation of a portion of the anisotropic pattern. This interpretation is further strengthened in the case of $SrCl_2:Sc^{2+}$ by the observation of a predicted anisotropy in the "averaged" spectrum. The effective-Hamiltonian parameters for $SrCl_2:La^{2+}$, $SrCl_2:Y^{2+}$, and $SrCl_2:Sc^{2+}$ are analyzed in terms of crystal field theory modified to include a weak to moderate vibronic interaction, i.e., a dynamic Jahn–Teller effect.

I. INTRODUCTION

For a nonlinear polyatomic complex Jahn and Teller[1] have shown that the orbital electronic degeneracy permitted by a symmetric nuclear configuration is incompatible with the stability of the symmetric configuration since asymmetric distortions remove the degeneracy and lower the energy of the system. For high-symmetry complexes in solids, e.g., ions with a d^1 configuration in eight-coordinated cubic sites, this instability is a result of the interaction between lattice vibrations and the electrons located on the ions. This vibrational-electronic or vibronic interaction determines the nature and the degeneracies of the states of the complex, both of which will generally be different from the results for the electronic states in the absence of the vibronic interaction. This subject has been extensively investigated theoretically.[2–4] When sufficiently strong, the vibronic interaction together with internal strains can produce a stable spontaneous distortion of the nuclear configuration to a symmetry sufficiently low to remove all orbital degeneracy, i.e., a "static" Jahn–Teller effect. However, even when the vibronic interaction is relatively weak, it produces pronounced effects on the matrix elements of certain vibronic operators and hence on certain experimental parameters, i.e., a "dynamic" Jahn–Teller effect. Since the existence of a significant vibronic interaction in-