ANOMALOUS DAMPING OF VOLUME PLASMONS IN POLYCRYSTALLINE METALS*

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Festenberg's observations of anomalously large damping of long-wavelength volume plasmons in a polycrystalline metal appear to be understandable in terms of plasmon scattering on the space-varying structure of the metal. A quantitative theory of this process involving the assumption of a random model for the structural configuration of the medium seems to describe the measurements satisfactorily.

Festenberg[1,2] has carried out a series of elegant measurements of the half-width ΔE of volume-plasmon energy losses by 50-keV electrons in polycrystalline foils of aluminum metal. The experiments were done for various known angular deflections θ of the fast electron and for foils composed of various crystallite sizes. He found that when foils are used for which the crystallite dimensions are $\gtrsim 250$ Å, the values for ΔE vs θ are described quite well by the free-electron-gas theory of Ninham, Powell, and Swanson[3]; a constant must be added to their theoretical damping values to account for Drude-type processes involving thermal effects, disorder, interband effects, etc. When crystallites of smaller dimensions were involved, a strongly augmented damping was observed in the region of small angular deflections ($\theta \lesssim 1$ mrad). This contribution decreases monotonically to zero at a rather steep rate as θ increases, beginning at a value for $\theta = 0$ which may be several times larger than the comparable damping in a foil composed of large crystallites. This grain-size–dependent damping seems to be unexplained to date.

A possible explanation of this phenomenon is presented herewith. One argues that a polycrystalline metal may be regarded as a random assemblage of crystallites in electrical contact over portions of their surfaces, but separated by regions having electronic composition different from that of the bulk metal. The interstices may be vacant or partially filled with smaller aggregates of matter. In a homogeneous isotropic electron gas the momentum of a plasmon is a constant of the motion. By contrast, if the system is weakly inhomogeneous the plasmon may scatter elastically on inhomogeneities from an initial state of given momentum to any of a large number of states of different momenta on the energy shell. This scattering should evince itself as lifetime broadening of a plasmon state created by a fast electron. We suggest that plasmon damping in polycrystalline media may be due in part to such scattering processes.

It is convenient to assume that the density inhomogeneities are weak and strictly random in character. We set the electron density at $\vec{r}$, $n(\vec{r}) = n_0 + \delta n(\vec{r})$, where $|\delta n(\vec{r})|/n_0 \ll 1$. Using this model, we give below an expression for the augmented volume-plasmon damping rate.

Note that elastic scattering of normal surface plasmons on static electron density fluctuations is known to occur in thin planar metallic plasmas. Relevant experimental data were first obtained by Brambring and Raether[4,5] and a successful interpretation on the basis of elastic scattering on surface roughness was proposed by Stern.[6] Wilems and one of us[7] have applied a quantum-hydrodynamical theory to this process with results equivalent to those of Stern. They suggested that volume inhomogeneities might be responsible for such interactions, as well as for interactions between photons and tangential surface plasmons.[8]

In the quantum-hydrodynamical model of a weakly inhomogeneous plasma system[8] the interaction of plasmons through static density variations (SDV) is described by the Hamiltonian $H' = \frac{1}{2}m^* n_0 \int d^3n f(\vec{r}) \vec{v}_{\rm op}^{\,2}$, where $\vec{v}_{\rm op}$ is the velocity operator for the bulk-plasmon field in a uniform isotropic electron gas of density n_0, $f(\vec{r}) = \delta n(\vec{r})/n_0$, and m^* is the effective electron mass.[9] If $b_{\vec{q}}^{\dagger}$ is the creation operator for a plasmon of wave vector $\vec{q}$, one may write

$$\vec{v}_{\rm op} = \sum_{\vec{q}} \left[\frac{2\pi\hbar e^2}{(m^*)^2 \omega_q \Omega}\right]^{1/2} \hat{q} e^{i\vec{q}\cdot\vec{r}} (b_{\vec{q}} + b_{-\vec{q}}^{\dagger}),$$

where $\hat{q} = \vec{q}/|\vec{q}|$, and $\omega_q \approx [\omega_p^2 + \frac{3}{5} v_F^2 q^2]^{1/2}$ is the frequency of a volume plasmon with wave vector $\vec{q}$. Also, $\omega_p^2 = 4\pi n_0 e^2/m^*$, and v_F is the Fermi speed of the electron gas.

Computing the damping rate γ of a plasmon in an initial state characterized by wave vector $\vec{q}_0$ due to elastic scattering on SDV by applying first-order perturbation theory and summing over possible final states characterized by wave vector $\vec{q}_f$, we find

$$\gamma = \frac{\pi\omega_p^2}{2\Omega^2}\sum_{\vec{q}_f}(\hat{q}_0\cdot\hat{q}_f)^2|f_{\vec{q}_0-\vec{q}_f}|^2\delta(\omega_{q_0}-\omega_{q_f}), \tag{1}$$

where $f_{\vec{k}} \equiv \int d^3r\, e^{i\vec{k}\cdot\vec{r}} f(\vec{r})$. Note that $|f_{\vec{k}}|^2$ is related to the x-ray scattering factor for the material under consideration. Performing an ensemble average, we may write $\Omega^{-1}\langle|f_{\vec{q}}|^2\rangle = \langle f^2\rangle\tilde{G}(\vec{q})$, where $\langle f^2\rangle$ is the mean square SDV averaged over the whole system, and $\tilde{G}(\vec{q})$ is the Fourier-transformed autocorrelation function. To simplify the analytical work, we use an isotropic Gaussian autocorrelation function[8]; then $\hat{G}(\vec{q}) = \pi^{3/2}\sigma^3 \times e^{-(\sigma q/2)^2}$, where σ is an autocorrelation length. Summing over final states on the energy shell we obtain

$$\frac{\gamma}{\omega_p} = \frac{5}{12}\left[\frac{\pi}{2}\right]^{1/2}\langle f^2\rangle\left(\frac{\sigma\omega_p}{v_F}\right)^2 g(\tfrac{1}{2}\sigma q_0), \tag{2}$$

where $g(x) \equiv x^{-5}[(2-2x^2+x^4)-(2+2x^2+x^4)e^{-2x^2}]$.

This result may also be obtained by generalizing a formula derived by Ferrell[10] for the damping of a (zero-momentum) electromagnetic wave in an electron gas containing an assembly of weak scattering centers. To compare the two models, we suppose that the ionic system of the polycrystalline material may be described by an ionic pseudopotential distribution $\mathcal{V}(\vec{r}) = \mathcal{V}_0(\vec{r}) + \delta\mathcal{V}(\vec{r})$, where $\mathcal{V}_0(\vec{r})$ is the distribution for a monocrystal of aluminum, and $\langle|\delta\mathcal{V}(\vec{r})|\rangle/\langle\mathcal{V}_0(\vec{r})\rangle \ll 1$, where the indicated averages are understood to be carried out over regions with dimension large compared with the average lattice spacing. We imagine that a plasmon propagating in the medium gives rise to an electric field $\vec{E}(\vec{r},t) = \hat{q}_0 E_0\cos(\vec{q}_0\cdot\vec{r}-\omega_{q_0}t)$. In the steady state this oscillatory electric field corresponds to harmonic motion of all electrons in the electron gas about their undisturbed positions. In this model the amplitude of the displacement vector at $(\vec{r},t)$ is $\vec{\xi}(\vec{r},t) = (e/m^*\omega_{q_0}^2)\vec{E}(\vec{r},t)$. The rate of energy loss from the plasmon field due to the motion of the electron gas relative to the positive ions may be computed from a semiclassical dielectric approach.[10] Dividing by $\Omega E_0^2/8\pi$, the average energy residing in the plasmon field, we find the damping rate to be

$$\gamma_{\rm tot} = \frac{e^2}{(m^*)^2\omega_{q_0}^2}\frac{1}{\Omega^2}\sum_{\vec{q}_f}(\hat{q}_0\cdot\hat{q}_f)^2\,\mathrm{Im}\left(\frac{-1}{\epsilon_{q,\,\omega_{q_0}}}\right)\times|q^2\mathcal{V}_{\vec{q}}|^2, \tag{3}$$

where $\vec{q} = \vec{q}_0 - \vec{q}_f$ and $\mathcal{V}_{\vec{q}} = \int d^3r\, e^{i\vec{q}\cdot\vec{r}}\mathcal{V}(\vec{r})$. Note that if we set $\sigma_1(\omega_{q_0}) = \gamma/\omega_{q_0}$ and let $\vec{q}_0 \to 0$, $\omega_{q_0} \to \omega_0$, $e\mathcal{V}_{\vec{q}} \to \mathcal{V}_{\vec{q}}\Omega$, we obtain Ferrell's equation for the transverse conductivity of the system. The Lindhard dielectric constant is denoted by $\epsilon_{q,\,\omega}$. In Eq. (3) we may put $\mathcal{V}_{\vec{q}} = \mathcal{V}_{0\vec{q}} + \delta\mathcal{V}_q$, where $q^2\delta\mathcal{V}_q$ is the Fourier-transformed ionic-charge-density fluctuation function. This quantity, when averaged over distances large compared with the Thomas-Fermi screening length but small compared with the grain sizes, may be set equal to $4\pi e n_0 f_{\vec{q}}$, which in turn is proportional to the electron-density fluctuation function. Ensemble averaging and neglecting the term involving $\mathcal{V}_{0\vec{q}}$, since we are not interested here in processes occurring in large crystals, we find the damping rate due to the polycrystalline structure to be

$$\gamma = \frac{\omega_p^4}{\Omega^2\omega_{q_0}^2}\sum_{\vec{q}_f}(\hat{q}_0\cdot\hat{q}_f)^2\,\mathrm{Im}\left(\frac{-1}{\epsilon_{q,\,\omega_{q_0}}}\right)|f_{\vec{q}}|^2. \tag{4}$$

This formula shows a contribution from single-particle damping processes[11] and a contribution which comes from plasmon creation; only the latter is to be compared with the quantum-hydrodynamical result given above. To make the comparison complete, we may set $\mathrm{Im}(-1/\epsilon_{q,\,\omega}) \simeq \frac{1}{2}(\pi\omega_p)\delta(\omega-\omega_q)$ in the region $(\omega_q/\omega_p - 1) \ll 1$; the latter restriction is implicit in the hydrodynamical treatment. With these substitutions Eq. (4) reduces to Eq. (1).

In Fig. 1 we compare the increase in damping rate due to crystallite size from Festenberg's data with the predictions of Eq. (2) above, both as a function of the angle θ. The experimental data were obtained from Fig. 5 of Ref. 2 and represent the difference in the damping half-width between Festenberg's solid points, obtained for nominally 70-Å crystallite size, and the open circles representing the energy half-width appropriate to large crystallites. These differences are plotted as the solid circles in Fig. 1. The solid theoretical curve is normalized to the point at $\theta = 0$ and is obtained by taking $q_0 = [(\omega_p/v)^2 + (k\theta)^2]^{1/2}$, where v is the velocity of the 50-keV

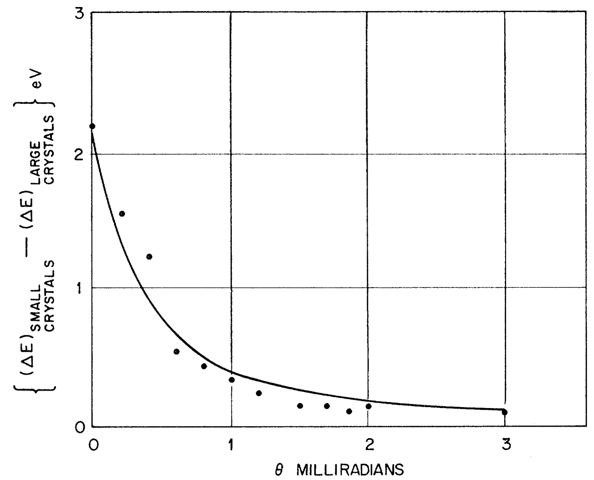

FIG. 1. Augmented plasmon damping width due to the polycrystalline structure of aluminum metal. The points were taken from Festenberg's data (Ref. 2, Fig.5). The smooth curve was calculated from Eq. (2).

electron and k is its wave number.

This fit was obtained by taking $\sigma \simeq 210$ Å which is three times as large as the crystallite size d inferred by Festenberg for this material. He obtained d from angular width $\Delta\theta$ of the (111) interference fringes by setting $d = \lambda_{el}/\Delta\theta$, where λ_{el} is the wavelength of the primary electron. It does not seem possible to match the steep decrease of the experimental values in the region $0 \le \theta \le 0.5$ mrad by setting $\sigma \simeq d$. Some of the discrepancy may be due to the fact that the uncertainty in the points obtained from Festenberg's data increases with θ, since one works with small differences between damping values, each of which is subject to experimental uncertainty, when $\theta \gtrsim 1$ mrad.

Augmented damping at small θ could occur through compound scattering processes involving elastic scatter of the fast electron on the polycrystallite structure plus inelastic encounters resulting in plasmon excitation; the composite process might involve two fairly large-angle scatters (several milliradians each) such that the intrinsic lifetime of the plasmon generated is large but the net angular deflection after the double scattering is small. Such processes do not appear to be important in Festenberg's experiments.[12] In any case it seems rather unlikely that composite scattering processes would give a damping curve so strongly peaked in the region $\theta \sim 0$. Another possibility is that the first-order perturbation theory used here is not sufficient to describe accurately the plasmon scattering process. Work is under way to extend the present theory to second order.

We note that Festenberg's technique may be quite useful in studying the long-range electronic structure of polycrystalline metals as well as that of other condensed matter. The volume plasmon may be a potentially valuable diagnostic probe of certain kinds of matter in a sense comparable with the x ray and the fast electron.

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[9]Note that a term in the interaction Hamiltonian which involves the pressure energy of the electron gas has been omitted here. One may show that there is a negligibly small contribution from this term under conditions which obtain in the Festenberg experiments.

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[11]One may show easily that these processes, which correspond to regions in the (q, ω) plane for which $\mathrm{Im}\epsilon_{q,\omega} \neq 0$, introduce negligible damping compared with the contribution from plasmon creation in the Festenberg experiments.

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