Coherent Double-Plasmon Excitation in Aluminum

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We report on coherent double-plasmon excitation in solid-state plasmas. Our results, obtained by use of a new processing routine for removal of incoherent plural scattering from energy-loss experiments on aluminum thin films, call into question previous theoretical and experimental findings as to the magnitude of the coherent double-plasmon excitation.

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Double-plasmon excitations are commonly found in electron energy-loss spectra (EELS) obtained in transmission experiments on thin metallic films and in x-ray emission spectra of solids. Double-plasmon satellites in x-ray emission spectra occur when the valence electron, before filling the vacant core level, excites two quanta of collective oscillation. The intensity F_2 of the double plasmon measured relative to the single-plasmon intensity in metals is of the order of some percent in the x-ray case.[1] In EELS experiments intensities of some ten to some hundred percent are found, depending on the thickness of the specimen.[2] This is because the fast electron traversing the specimen in an EELS experiment interacts a number of times with the solid-state plasma; in each interaction along its trajectory it will lose the plasmon excitation energy E_p with a high probability, and hence the EEL spectrum will exhibit a number of peaks at the multiples of the single-plasmon excitation energy. The peak intensities obey a Poisson distribution.[2,3]

Ashley and Ritchie[4] were the first ones who considered the possibility of the excitation of *two* plasmons in a single interaction of the fast probe electron with the solid-state plasma. This process should cause a subsidiary maximum in the EEL spectrum at the energy as the subsequent excitation of two single plasmons, viz., at $2E_p$. So it cannot be observed directly. Since the latter interaction is essentially an incoherent one, whereas the simultaneous excitation of two quanta of collective oscillation in one event corresponds to inclusion of second-order terms in a perturbation theoretical treatment of the solid-state plasma, we shall distinguish these cases by referring to *coherent* and *incoherent* excitations, in accordance with the notation of Faraci and Pennisi.[5]

Ashley and Ritchie originally calculated the relative probability F_2 for the coherent double-plasmon loss in the random-phase approximation (RPA). They found, assuming a plasmon cutoff wave number q_c of 1.1 Å^{-1} in aluminum, a relative intensity $F_2=0.04$. This value is very sensitive to the choice of q_c. A value of $q_c=1.5$ Å^{-1} yields[6] $F_2\simeq 0.17$. Srivastava *et al.*[1] predicted $F_2=0.024$ from a quantum-mechanical calculation based upon a canonical transform of the many-body Hamiltonian including second-order terms.

Not only theoretical predictions but also experimental results disagree by an order of magnitude (see Table I). The main problem here is to single out the coherent contribution from the much larger incoherent double-plasmon peak. Spence and Spargo[6] reported an experimental value of $F_2=0.13$ for coherent double-plasmon excitation in energy-loss spectra of an aluminum single crystal, a value higher than but not inconsistent with the prediction of Ashley and Ritchie.

Faraci and Pennisi[5] compared the dispersion of the double-plasmon maximum measured by Batson and Silcox[8] with Monte Carlo simulations of the incoherent process and found disagreement.

A straightforward way to obtain the coherent contribution experimentally is to process the spectra so as to remove plural incoherent events from measurements. When the thickness of the specimen does not exceed a few mean paths (MFP's) for plasmon-electron interaction, individual peaks in the energy range of plasmon and interband excitations can be discerned. The single-scattering probability f_1 is, however, masked by plural losses even for thicknesses less than one MFP. A scattering experiment always yields the plural-scattering probability p. The problem is how to retrieve f_1 from measurement of p.

TABLE I. Excitation probability F_2 of the coherent double-plasmon event.

Authors	Method	F_2 (%)	Thickness (MFP)
Ashley and Ritchie[a]	Theory	4–17	···
Srivastava *et al.*[b]	Theory	2	···
Misell and Atkins[c]	Image mode	≤ 2	0.5–0.8
Spence and Spargo[d]	Image mode	13	0.03–2.3
Batson and Silcox[e]	Diffraction mode	7	0.7–1.4
Present	Diffraction-image mode	≤ 0.5	0.5–1.0

[a]Reference 4.
[b]Reference 1.
[c]Reference 7.
[d]Reference 6.
[e]Reference 8.

A number of methods have been reported in the literature for retrieval of the single-loss probability. Some of them are suited for EEL spectra obtained in the electron microscope in *image mode,* i.e., when all electrons independent of their angle of scattering are collected.[9] More recently, methods have been used which work in *diffraction mode.*[10] In the latter case, the scattering probability $p=p(E,\vartheta)$ is measured in the focal plane of the objective lens as a function of energy loss E and scattering angle ϑ.

By use of these methods for image-mode spectra of aluminum, F_2 was found to be less than 0.02 after the correction for incoherent double losses.[7] This value is close to the prediction of Srivastava *et al.*[1]

Batson and Silcox[8] found $F_2\simeq 0.07$ after removal of plural incoherent losses in diffraction-mode energy-loss spectra of aluminum.

In an attempt to reconcile these contradictory results we investigate diffraction-mode EEL spectra of aluminum. For processing, we use a newly developed closed procedure capable of retrieving angle-resolved single-inelastic-scattering profiles from energy-loss measurements.[11,12]

The task is accomplished by the calculation of matrices

$$\mathbf{A}_l = D^{-1}[(\mathbf{C}_l-\mathbf{1})-\tfrac{1}{2}(\mathbf{C}_l-\mathbf{1})^2 + \tfrac{1}{3}(\mathbf{C}_l-\mathbf{1})^3-\cdots], \quad (1)$$

where the entries of the matrices $\mathbf{A},\mathbf{C}$ are defined respectively as

$$A_{l,ij}=\int_{E_{i-j}-\Delta E/2}^{E_{i-j}+\Delta E/2} dE \int d^2\Omega f_1(E,\vartheta)P_l(\cos\vartheta) \quad (2)$$

and

$$C_{l,ij}=\int_{E_{i-j}-\Delta E/2}^{E_{i-j}+\Delta E/2} dE \int d^2\Omega p(E,\vartheta)P_l(\cos\vartheta). \quad (3)$$

P_l are Legendre polynomials, $\mathbf{1}$ is the unity matrix of same order as $\mathbf{C}_l$, and E_i is the energy loss at the ith channel in the spectrum which starts at $E_0=0$. The order of matrices is given by the number of channels. After calculation of $\mathbf{C}_l$ by Eq. (3), $\mathbf{A}_l$ are obtained from the logarithmic series expansion (1). The single-scattering probability $f_1(E,\vartheta)$ of Eq. (2) is then reconstructed from the $\mathbf{A}_l$ by a proper series in Legendre polynomials.

Measurements were done with a cylindrical-mirror analyzer (CMA) attached to a modified Siemens Elmiskop IA at 40-keV primary-beam energy. The energy resolution was typically 0.75 eV. In diffraction mode, energy scans were performed with an angular resolution of ± 0.17 to ± 0.80 mrad depending on condenser overfocus and camera length. The specimens were evaporated from a tungsten boat at 2×10^{-4} Pa onto glass substrate covered with Mowital. The deposition rate was $\simeq 0.5$ nm/s. The films were floated off the substrates in chloroform and prepared onto Cu grids. The spectra were smoothed with use of a cubic spline algorithm, and surface plasmon scattering was removed in a deconvolution process.

Typical diffraction-mode spectra of aluminum films of thickness 24 and 49 nm are shown in Figs. 1 and 2. Three graphs are superimposed on each diagram. The full line is the smoothed measured spectrum, corrected for surface plasmons. The dash-dotted line is the spectrum corrected for quasielastic (diffuse) and small-angle elastic plural scattering. Not only is the secondary peak corresponding to superposition of the image-mode spectrum done away with, but also the maximum of the main

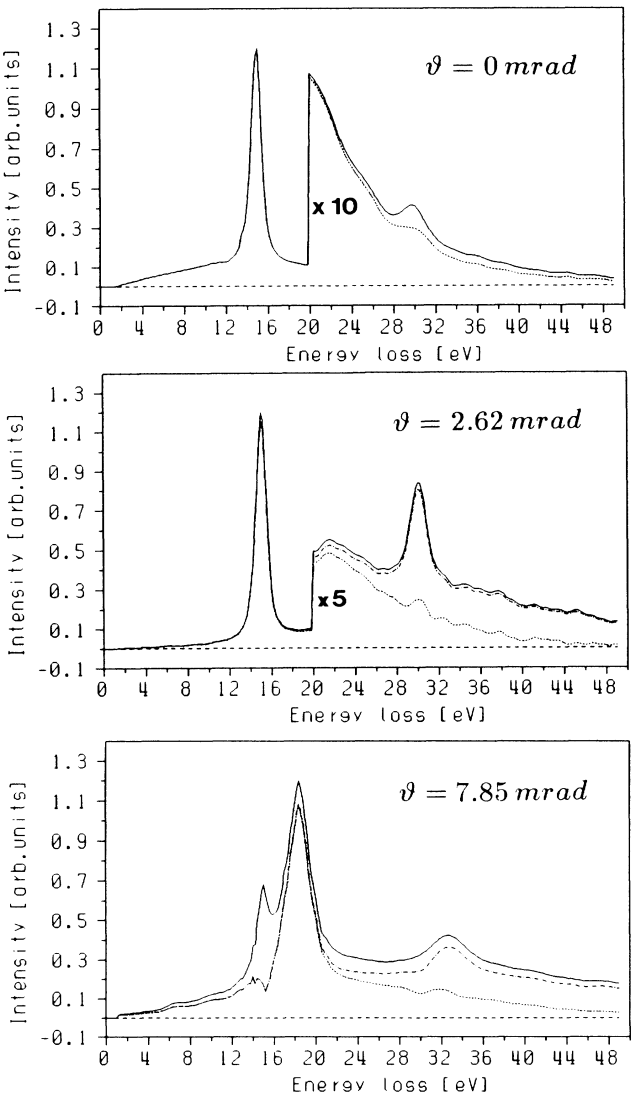

FIG. 1. Diffraction-mode energy-loss spectra at various scattering angles for a 24-nm Al film: solid lines, measured; dash-dotted lines, corrected for elastic plural scattering; dashed lines, single loss. Parts of the drawings are magnified for clarity.

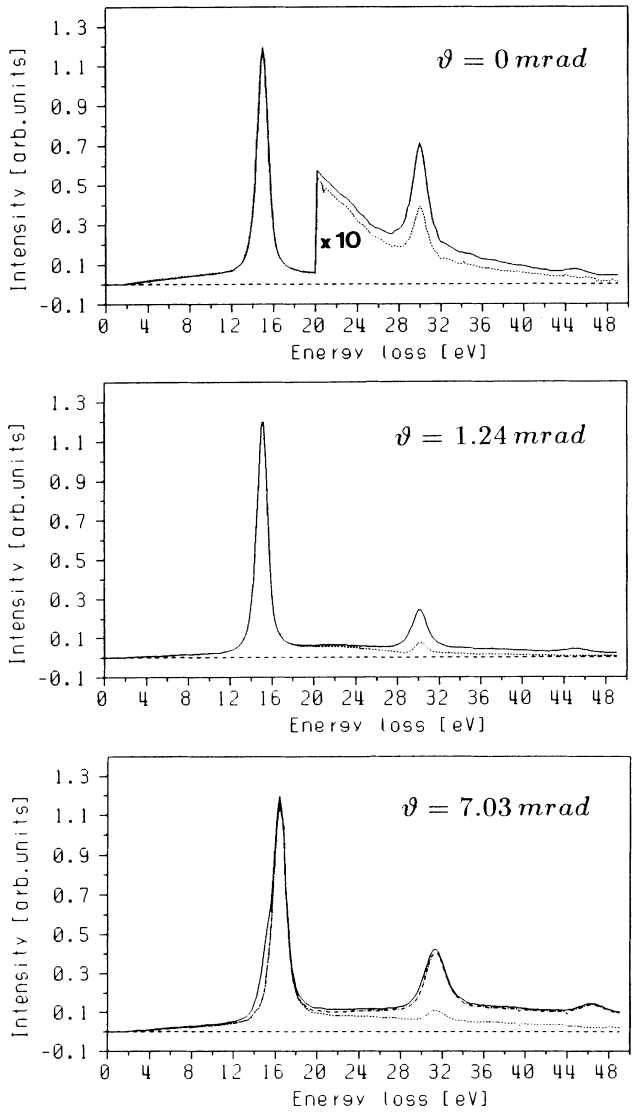

FIG. 2. Same as in Fig. 2 for a 49-nm Al film. Scattering angles are different from those in Fig. 1.

peak is slightly reduced in the graphs for the higher scattering angles.

The dashed line marks the single scattering probability. Note the increase in reduction of intensity by deconvolution with energy loss, angle, and film thickness. Numerical details are published elsewhere.[13]

The third-plasmon peak at 45 eV in aluminum is completely removed; not so the double-plasmon peak at 30 eV. After the foregoing discussion, this peak is assigned to a coherent excitation of two plasmons. For the thin specimen, the area under this peak—taken from 28 to 33 eV—is of the order of 1% of the corresponding area under the single-plasmon maximum, almost independent of scattering angle. For the thicker specimen, the relative intensity is generally higher ($\simeq 1.3\%$ at small scattering angles and increasing to $\simeq 4\%$ for high scattering angles). The mean values of the relative intensities, averaged over ten energy scans between 0 and 12.9 mrad, are 0.0086 and 0.0221 for the 24- and 49-nm-thick specimens, respectively.

Double Bragg-inelastic scattering causes a small amount of incoherent double-plasmon intensity to remain at high scattering angles,[8] and so the coherent contribution is smaller than the observed values. This effect is more prominent the thicker the specimen. Hence, the most reliable result is that for the thinnest film at small angles. For the first four E scans, we obtain an average of 0.0039 and 0.0127. This result can be checked by comparison with results from deconvoluted image-mode spectra in which the processing should definitely remove all incoherent contributions. We obtain 0.0031 and 0.0032 for the two Al films. For the 24-nm film this is in satisfactory agreement with the above average. Obviously, in the 49-nm film Bragg scattering is responsible for a good deal of the remaining double-plasmon intensity in the diffraction-mode spectra even at the smallest angles.

The results of the deconvolution are sensitive to the height of the elastic peak. Underestimation of the peak height by 3% would yield $F_2 = 0.0053$. However, for $\simeq 10^6$ counts at the elastic peak, the counting statistics is $\simeq 0.1\%$. Detector saturation effects are in order of 1% in the present experiments. So, underestimation of the elastic peak is improbable, the more so as it would be counterbalanced by "wrong" additional intensity from thinner parts or even small holes in the specimen. The fact that we obtain very similar values for F_2 from image-mode spectra of both specimens is also a strong indication for absence of experimental or numerical errors.

From our experiments, we impose an upper limit of $F_2 = 0.005$ onto the coherent double-plasmon excitation probability. The higher values for F_2 previously reported (see Table I) may be due to the use of less sophisticated processing,[7,8] or of thicker films[7] in which Bragg inelastic scattering is a serious problem, and to investigation of single crystals,[6] in which dynamical effects may enhance the probability for coherent double-plasmon excitation.

Further EELS experiments with simple metals in combination with exact processing routines which are now operational should yield more information on the existence, strength, and dispersion of the coherent double plasmon.

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