Measurement of Surface Plasmon Dispersion in Aluminum and Indium*

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Energy-loss experiments with 50-keV electrons on thin polycrystalline films of Al and In yielded data for the surface plasmon dispersion up to $k_{\parallel}=0.47$ and 0.42 Å^{-1}, respectively. The wave-vector dependence of the surface plasmon frequency of Al shows a significant increase for $k_{\parallel}>0.3$ Å^{-1}, while in the case of In there is only a weak increase for $k_{\parallel}>0.2$ Å^{-1}.

Experimentally and theoretically it is well established that the frequency of surface plasmons (SP) is dependent on the momentum transfer parallel to the surface $\hbar k_{\parallel}$ and decreases to zero as $k_{\parallel}\to 0$ due to retardation. For larger $k_{\parallel}$ values $k_p<k_{\parallel}\ll k_F$, where $k_p=\omega_p/c$, with ω_p the plasma frequency and k_F the Fermi wave vector, the frequency approaches $\sim\omega_p/\sqrt{2}$ for a clean-vacuum–free-electron-gas boundary. In the region of higher $k_{\parallel}$ values, where retardation can be neglected ($k_{\parallel}\gg k_p$), several theoretical attempts have been made to calculate the surface plasmon dispersion. Early work predicts an increase of the frequency due to thermal motion of the plasma electrons[1,2]; and subsequent studies show that the shape of the electron density profile at the surface has a strong influence on the $\omega(k_{\parallel})$ dependence.[3-9] The situation has been reviewed quite recently in Ref. 9. There are mainly two experimental approaches to observe the surface plasmon dispersion: inelastic low-energy electron diffraction (ILEED) and high-energy electron loss spectroscopy (in transmission). The results which shall be described in the following have been obtained with the second method.

Electrons with kinetic energies E_0 (50 keV in these experiments) and momenta $\hbar k_0$ pass through thin films several 100 Å thick. They are scattered inelastically into angles θ losing energies $\Delta E\ll E_0$ and transferring momenta $\hbar k$ to the foil. The momentum transferred to the surface in the case of normal incidence of the incoming electrons amounts to $k_{\parallel}=k_0\theta$. The dispersion is measured observing the value $\Delta E_s=\hbar\omega_s$ of the surface loss as a function of momentum transfer $\hbar k_{\parallel}$ or of the scattering angle θ.

Earlier experiments on Mg[10,11] and on Al[11,12] yielded results out to values of $k_{\parallel}\sim 0.3$ Å^{-1}. Several improvements of the apparatus described in Ref. 12 (e.g., better beam stability and a more sensitive detection system) made it possible to observe the SP dispersion of Al out to $k_{\parallel}=0.47$ Å^{-1} and that of In out to $k_{\parallel}=0.42$ Å^{-1}. The energy half-width of the primary beam and the angular width were 0.5 eV and $(2-2.5)\times10^{-4}$ rad, respectively, for all measurements. In order to determine the position of the surface peak, its intensity should be sufficiently high at large θ values to separate it from the low-energy wing of the volume loss. However, there is a limiting factor since the surface-loss intensity decreases strongly with θ, namely, with θ^{-3}, whereas that of the volume excitation decreases with θ^{-2}. This difficulty can be compensated to a certain extent by using thin films so that the intensity of the volume loss can be reduced and becomes comparable with the intensity of the surface loss, which is nearly independent of the thickness. A thickness of about 300 Å gives good results for both Al and In.

Since the position of the surface loss is sensitive to contamination of the metal surface, the sample has been prepared under ultrahigh-vacuum conditions ($\sim 3\times10^{-9}$ Torr). To reduce the rate of contamination during electron irradiation, a cooling trap filled with liquid N_2 surrounded the film. The cleanliness of the surface has been controlled during measurements by determining the position of the surface loss at $\theta=0$ from time to time. Thin substrates were necessary to support the metal films. To obtain the metal loss spectrum, the contribution of the substrate loss spectrum has to be considered. Since its structure depends also on k, the loss spectrum was determined as a function of k before depositing the metals and subtracted from the metal-plus-substrate spectrum recorded at different wave vectors. The substrate materials were films of SiO for In and carbon for Al about 150 Å thick. The characteristic energy-loss spectra for both materials show only a weak structure at ΔE values rather different from that of the metals; this is valid for In on SiO up to $k_{\parallel}\sim 0.4$ Å^{-1}. The metal films deposited on these substrates by vaporization were polycrystalline.

The Al spectra show two separate excitations due to the two interfaces, vacuum/Al ($\sim$10.2 eV)

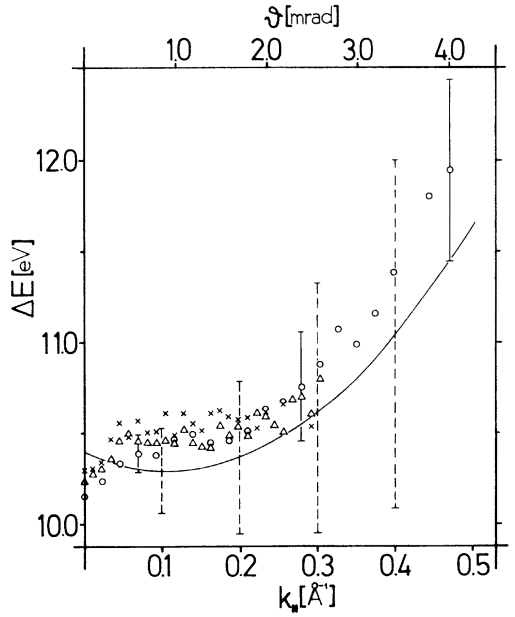

FIG. 1. Dispersion of the surface-plasma loss of Al. Results from high-energy electron energy-loss experiments by Kloos and Raether, Ref. 11 (crosses), by Langkowski, Ref. 12 (triangles), and from present work (circles). Dispersion curve derived from ILEED measurements by Duke *et al.*, Ref. 17 (full line).

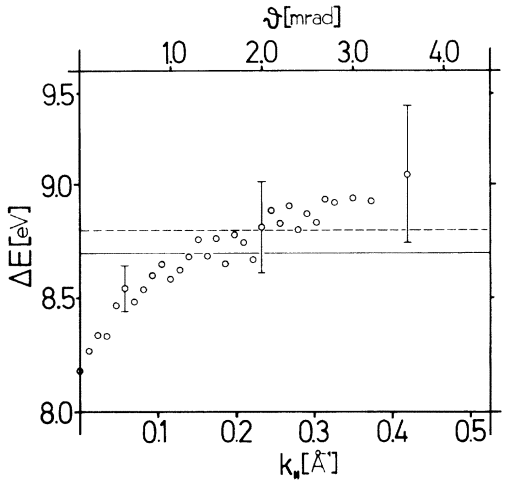

FIG. 2. Dispersion of the surface-plasma loss of In. Measured values (open circles); Value of the surface plasmon frequency derived from optical-reflection experiments by Koyama, Smith, and Spicer (Ref. 18) and value obtained from electron-energy-loss reflection experiments by Schilling, Ref. 19 (full line).

and Al/carbon (~7.4 eV).[13,14] The dependence of the ~10-eV loss on the momentum transfer has been observed and is plotted in Fig. 1 together with earlier energy-loss data obtained with 50-keV electrons. The results of these experiments are in agreement within the limits of accuracy. For wave vectors $k_{\parallel}>0$ and 2 Å^{-1} a slight increase of ΔE_s with $k_{\parallel}$ takes place, indicated in the data of Ref. 12 too, but not exceeding the limits of accuracy. This tendency becomes significant for $k_{\parallel}$ >0.3 Å^{-1}; ΔE_s increases to 11.95 ± 0.5 eV at $k_{\parallel}$ $=0.47$ Å^{-1}. The indicated error bars are a consequence of the poor intensities of the surface plasmon excitation at high $k_{\parallel}$ values. The results on Al demonstrate a pronounced increase of the frequency of the surface plasmon with $k_{\parallel}$. A theoretical evaluation of this result cannot be made for the moment since the theoretical situation is not yet settled.

ILEED experiments on the SP dispersion of Al have been performed.[15,16] The recent data on Al(100) of Duke *et al.*[17] and the corresponding error bars have been plotted in Fig. 1 showing an agreement in the general behavior concerning the increase of the surface plasmon frequency with $k_{\parallel}$. One has to keep in mind that the ILEED data are obtained on single crystals whereas ours have been measured on polycrystalline films deposited by evaporation. The measured dispersion is therefore averaged over the different crystal directions. For a detailed comparison with ILEED data it would be necessary to calculate a dispersion relation averaged over all crystal directions, which is not available. Furthermore, we can say that our data exclude a negative slope of the dispersion curve. For a more detailed discussion, however, the accuracy of the experimental results has to be improved.

For In it was possible to measure the SP dispersion up to $k_{\parallel}=0.42$ Å^{-1}. For higher values of $k_{\parallel}$, contributions of the characteristic energy-loss spectrum of SiO (weak structures in the region of the surface excitation of In) to the energy-loss spectrum appear, thus precluding a reliable determination of the surface excitation of In. Therefore, the results on In are plotted only up to $k_{\parallel}=0.42$ Å^{-1} (Fig. 2). The result is found to be different from that for Al. Beyond the retardation region only a slight increase of ΔE_s with $k_{\parallel}$ takes place. For the interpretation of the differing results on Al and In, one has to take into account the different bulk electron densities of these materials which may influence the electron density distribution at the surface. Furthermore, an influence of surface roughness on the SP dispersion by changing the effective electron density distribution at the surface has to be considered. At the moment, however, a more detailed dis-

cussion of this problem is premature.

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[1]H. Kanazawa, Prog. Theor. Phys. 26, 851 (1961).
[2]R. H. Ritchie, Prog. Theor. Phys. 29, 607 (1963).
[3]A. J. Benett, Phys. Rev. B 1, 203 (1970).
[4]Ch. Heger and D. Wagner, Z. Phys. 244, 449 (1971).
[5]J. Harris, J. Phys. C 5, 1757 (1972).
[6]J. Heinrichs, Phys. Rev. B 7, 3487 (1973).
[7]D. E. Beck and V. Celli, Surf. Sci. 37, 48 (1973).
[8]P. J. Feibelman, Phys. Rev. B 9, 5077 (1974).
[9]A. D. Boardman, B. V. Paranjape, and R. Teshima, Surf. Sci. 49, 275 (1975).
[10]C. Kunz, Z. Phys. 196, 311 (1966).
[11]T. Kloos and H. Raether, Phys. Lett. 44A, 157 (1973).
[12]J. Langkowski, cited by H. Raether, in *Proceedings of the Fourth International Conference on Vacuum Ultraviolet Radiation Physics, Hamburg, 1974*, edited by E. E. Koch, R. Haensel, and C. Kunz (Pergamon, New York, 1974), p. 597.
[13]T. Kloos, Z. Phys. 265, 225 (1973).
[14]P. Schmüser, Z. Phys. 180, 105 (1964).
[15]C. B. Duke and U. Landman, Phys. Rev. B 8, 505 (1973).
[16]J. O. Porteus and N. W. Faith, Phys. Rev. B 12, 2097 (1975).
[17]C. B. Duke, L. Pietronero, J. O. Porteus, and J. F. Wendelken, Phys. Rev. B 12, 4059 (1975).
[18]R. Y. Koyama, N. V. Smith, and W. E. Spicer, Phys. Rev. B 8, 2426 (1973).
[19]J. Schilling, Z. Phys. B25, 61 (1976).

Spin-Flip Raman Echo in *n*-Type CdS

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We report on the first observation of a Raman echo, using spin-flip Raman scattering at 4905 Å of bound donors in CdS to create a coherent spin state. The free-induction decays associated with each pulse in the sequence of two $\pi/2$ pulses as well as the echo are probed by spin-flip Raman scattering at 4880 Å.

A powerful tool for studying the microscopic or irreversible phase memory time of any two-level system is the class of well-known spin[1] and photon echo experiments.[2] Since it has been demonstrated very early that coherent states can be prepared by stimulated Raman scattering or two-wave mixing,[3] it is to be concluded that an echo signal can be generated by either of these processes and is called a Raman echo.[4] However, while various other coherent phenomena involving two-photon process have recently been demonstrated,[5] we report here the first observation of a Raman echo.

Spontaneous[6] and stimulated[7] spin-flip scattering were first observed in InSb and later in CdS.[8,9] For two time-reversed states $|a\rangle$ and $|b\rangle$ [see Fig. 1(a)] split in a magnetic field along z by $\hbar\omega_{ba}$ and for cubic symmetry,[10] the effective spin-flip Hamiltonian $H_{sp}^{(2)}$ was first given by Yafet as[11-13]

$$H_{sp}^{(2)} = \tfrac{1}{2}\alpha\vec{\sigma}\cdot(\vec{E}_L \times \vec{E}_R) \times \exp[i(\omega_L - \omega_R)t - (\vec{k}_L - \vec{k}_R)\cdot\vec{r}] + \text{c.c}, \quad (1)$$

where $\vec{E}_L$ is the laser field and $\vec{E}_R$ the Raman field with angular frequencies ω_L, ω_R and wave vectors $\vec{k}_L, \vec{k}_R$, respectively; $\vec{\sigma}$ are the Pauli matrices; $\vec{r}$ is the position vector of the impurity in the crystal; and α is related to the spontaneous differential Raman cross section $d\sigma/d\Omega$ by[12] $d\sigma/d\Omega = 4|\alpha|^2(\omega_L + \omega_{ba})^3\omega_L/c^4$. α becomes very large when $\hbar\omega_L$ is near-resonant to an excited state, which is the exciton bound to a neutral donor in our case.[8] Since in Eq. (1), $\alpha(\vec{E}_L \times \vec{E}_R)\exp[i(\omega_L - \omega_R)t]$ acts as an effective resonant rf magnetic

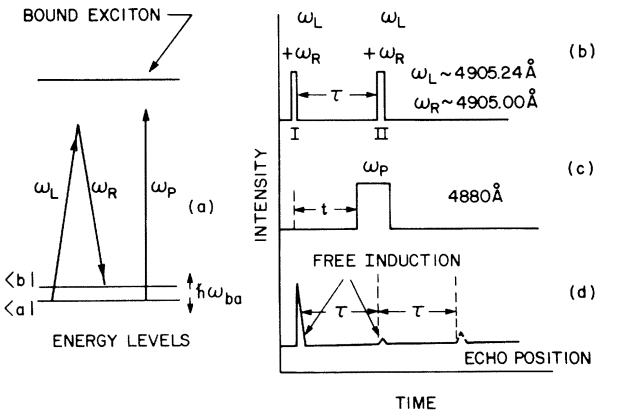

FIG. 1. (a) Energy levels in a Raman echo experiment. The excited state here is an exciton bound to a neutral donor. (b) The excitation pulse sequence of the dye laser. (c) The argon probe timing. (d) Expected behavior of 4880-Å Stokes free-induction and echo signals.