Excitation of Surface Plasmons on He-Filled Cavities in Al

R. Manzke and G. Crecelius
Institut für Festkörperforschung, Kernforschungsanlage Jülich GmbH, D-5170 Jülich, Federal Republic of Germany
and
J. Fink
Institut für Nukleare Festkörperphysik, Kernforschungszentrum Karlsruhe, D-7500 Karlsruhe, Federal Republic of Germany

(Received 27 June 1983)

Surface plasmon losses excited on spherical, He-filled cavities in Al are studied with use of transmission electron energy-loss spectroscopy. It is found that the excitation energy of the $l = 1$ (dipole) surface plasmon mode decreases with increasing He concentration, in line with predictions of an effective-medium theory taking into account the dipole-dipole interactions between bubbles in dense populations, the density dependence of the He dielectric constant, and a density-dependent atomic polarizability of the He in the bubbles.

PACS numbers: 71.45.Gm, 61.70.Tm, 79.20.Kz

Collective electronic excitations on concave surfaces [void or bubble surface plasmons (BSP)] are a subject of great current theoretical interest.[1-10] In contrast, experimental data are rather scarce, primarily because of the lack of adequate, well characterized samples. Pioneering experiments have been performed on helium bubbles in an Al matrix by Henoc and Henry,[11] who observed bubble images using an energy-selective electron microscope, and about ten years later by Manzke and Campagna[12] and Rife *et al.*[13] with electron energy-loss spectroscopy (EELS). With use of He^+ implantation with variable energy and dose, dense, and homogeneously distributed bubble populations in Al films can be produced,[14] and it has been stated that on such samples several eigenmodes of the BSP are observable by EELS.[12] In this Letter, we report results of an experimental effort towards the systematic investigation of the $l=1$ (dipole) mode of the BSP in Al. The philosophy underlying this investigation is as follows: (1) With use of EELS, the excitation energy of both the $l=1$ mode of the BSP and the He 1^1S_0-2^1P_1 transition is measured for Al-He samples implanted to different He concentrations. (2) As the relation between the energy shift, ΔE, of the He transition with respect to its atomic value of 21.23 eV and the He density is well established,[14,15] the He density in the bubbles can be determined. (3) Using this, we show that the concentration dependence of the excitation energy of the BSP dipole mode is well described within the Maxwell-Garnett effective-medium theory.

Epitaxially grown Al films (1000 Å thick, grain sizes > 5000 Å) have been homogeneously populated with He bubbles to high bubble densities by subsequent implantation of He^+ ions with different energies, 0.5 keV $\leq E_{\rm ion} \leq$ 8 keV, and doses $\Phi_i(E_{\rm ion})$. The He concentration $C_{\rm He}$ in the samples has been determined by use of EELS in combination with proton-enhanced scattering (PES) experiments, described together with the trapping curve and the sample characterization elsewhere.[14,16] Here we use Al-He samples having a He concentration proportional to the implantation dose Φ $(=\sum\Phi_i)$. The shape of the bubbles is predominantly spherical.[14,16] The bubbles have a size distribution the width of which is about 6 Å for $C_{\rm He} \lesssim 16$ at.%. Locally ordered bubble arrangements are observed in these samples.[14,16] Transmission EELS was carried out with a high-resolution 170-keV spectrometer. The spectra were taken in the forward direction with an energy resolution of 130 meV and a momentum resolution of 0.1 Å^{-1}.

The EELS spectra of Al films implanted to different He concentrations $C_{\rm He}$ are shown in Fig. 1. The spectra are normalized with respect to the intensity of the Al volume plasmon loss. In addition to the single and double volume plasmons at 15 and 30 eV, respectively, and surface plasmons excited on the Al_2O_3-coated flat film surfaces, we find two additional excitations for the implanted samples which become more intense with increasing $C_{\rm He}$:

(1) In the high-energy regime we find the He 1^1S_0-2^1P_1 transition which is shifted by $\Delta E = 3.32$ eV for $C_{\rm He} = 3.3$ at.% with respect to the atomic

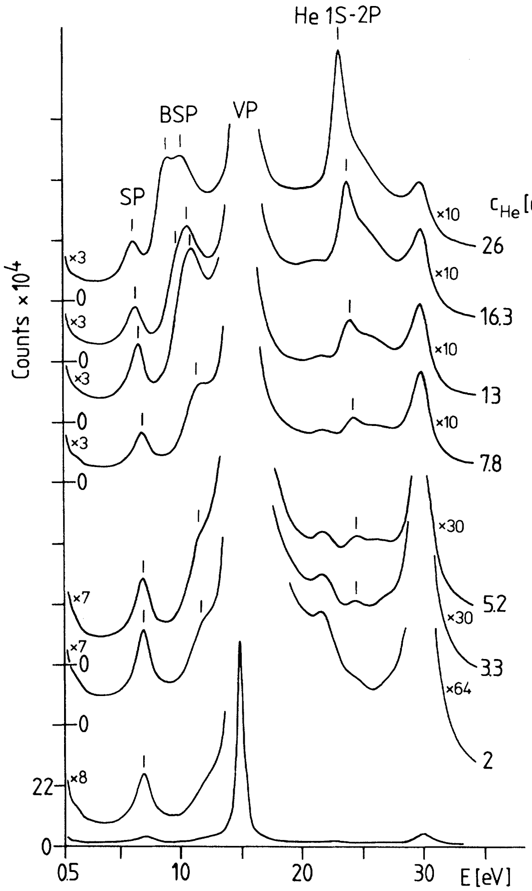

FIG. 1. EELS spectra of 1000-Å-thick Al films implanted to different He concentrations C_{He}. The spectra are taken in the forward direction and are normalized with respect to the intensity of the Al volume plasmon loss (VP). SP is the surface plasmon; BSP is the bubble surface plasmon. Additional structures are due to double scattering processes, e.g., the excitation of two Al volume plasmons at 30 eV (Ref. 16).

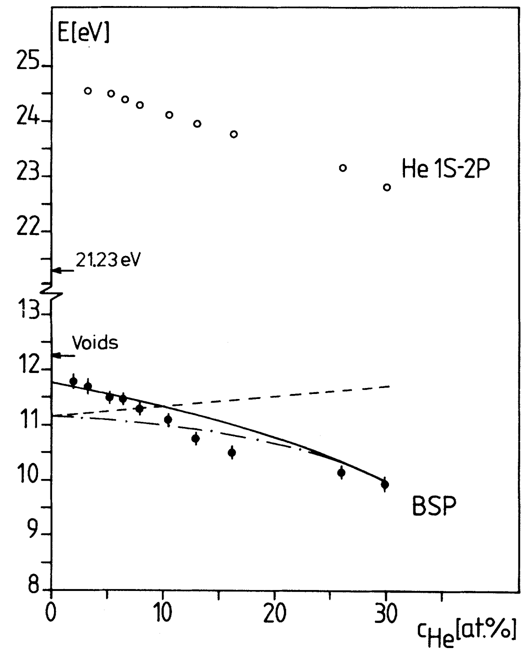

FIG. 2. He concentration dependence of the excitation energy of both the BSP dipole mode and the He $1S-2P$ transition. Note that the excitation energy of a surface plasmon dipole mode on an empty cavity is given by $\frac{2}{3}^{1/2}\hbar\omega_p = 12.3$ eV. Theoretical results: $f \ll 1$, $\alpha_0 = \text{const} = 0.205$ Å^3 (dashed line); f, $\alpha_0 = \text{const} = 0.205$ Å^3 (dash-dotted line); f, $\alpha_0 = \alpha_0(n)$ (solid line); see text.

excitation energy of 21.23 eV. This shift is due to the elevated He density in the bubbles.[13-15] With increasing C_{He} ΔE decreases whereas the intensity of the line increases. The latter has been used for the determination of C_{He} by EELS (for details see Ref. 16). ΔE is proportional to the He density,[15]

$$\Delta E/n = (24 \pm 5) \text{ eV Å}^3, \qquad (1)$$

in reasonable agreement with a previously published estimate.[13] Equation (1) will be used to determine the He density within the bubbles.

(2) In the low-energy regime we find the bubble surface plasmon loss. For low C_{He} only one loss is excited, due to the $l = 1$ (dipole) mode, because for 170-keV electrons and the bubble sizes with mean radii of $r = 6.5$ Å for $C_{He} = 3.3$ at.% and 10 Å for 13 at.%, the excitation probability[5] for modes $l > 1$ is negligible. For high C_{He} an additional structure is observed at the low-energy tail of the dipole mode, possibly due to the contribution of modes with $l > 1$ for these larger bubbles [$r = (20 \pm 8)$ Å for $C_{He} = 26$ at.%].

The excitation energies of both the BSP dipole mode, $\hbar\omega_{l=1}$, and the He $1S$-$2P$ transition are shown as a function of C_{He} in Fig. 2. The energy shift ΔE of the He $1S$-$2P$ transition and, according to Eq. (1), the He density within the bubbles decrease about linearly with increasing C_{He}. Likewise $\hbar\omega_{l=1}$ decreases with increasing C_{He}. Note that Natta's[1] equation for an isolated bubble, $(\hbar\omega_l)^2 = (\hbar\omega_p)^2(l+1)/[l(\epsilon+1)+1]$, predicts an increase of $\hbar\omega_{l=1}$ with decreasing n (increasing C_{He}), in contradiction with the experimental result. $\hbar\omega_p$ is the Al volume plasmon energy and $\epsilon = \epsilon_{He}$ is the dielectric constant of the He within the bubble. Thus, in addition to the change of the He density within the bubbles, an improved theoretical description also has to account for the consequences of a dense bubble population, namely, the long-range dipole interactions between the bubbles.

We describe the electronic properties of the Al/He-bubble system by an effective dielectric function $\bar{\epsilon}(\omega)$, as in the model proposed by Maxwell-Garnett[17] (MG) for small metallic particles in a dielectric host (effective-medium theory[18-20]):

$$\frac{\bar{\epsilon}(\omega)-\epsilon(\omega)}{\bar{\epsilon}(\omega)+2\epsilon(\omega)}=f\,\frac{\epsilon_{\rm He}(\omega)-\epsilon(\omega)}{\epsilon_{\rm He}(\omega)+2\epsilon(\omega)}, \tag{2}$$

strictly applicable for bubbles arranged in a cubic lattice. $\epsilon(\omega)$ describes the metal and $\epsilon_{\rm He}(\omega)$ the He dielectric function in the bubbles. The dense bubble population is taken into account by the increase of sample volume, ΔV, caused by the introduction of He bubbles—the filling factor:

$$f=\Delta V/V=4\pi n_B r^3/3=C_{\rm He}/n\Omega_{\rm Al}, \tag{3}$$

with n_B the volume density of the bubbles, r the mean bubble radius, and $\Omega_{\rm Al}$ the Al atomic volume. Thus, the MG theory considers that the local field acting on a bubble depends on the spatial location of the bubble but not on its shape and size. With use of Eq. (3) f can be determined from experimentally derived values (e.g., $f=1.4\%$ and 19% for $C_{\rm He}=3.3$ and 26 at.%, respectively).

The frequency-dependent dielectric function of Al is well approximated by that of a free-electron gas,

$$\epsilon(\omega)=1-\omega_p^{\,2}/(\omega^2+i\omega g), \tag{4}$$

with ω_p the plasma frequency and g a phenomenological damping.[21] The dielectric properties of the He are described by the Clausius-Mossotti formula:

$$\epsilon_{\rm He}(\omega)=1+4\pi n\,\alpha(\omega)/[1-4\pi n\,\alpha(\omega)/3], \tag{5}$$

where the frequency-dependent electronic polarizability is approximated by a Lorentz *Ansatz*, $\alpha(\omega)=\alpha_0\omega_0^{\,2}/(\omega_0^{\,2}-\omega^2-i\gamma\omega)$, with α_0 the atomic electronic polarizability of He and the He resonance at $\hbar\omega_0=21.23$ eV[22] damped by a constant γ.[21]

From $\bar{\epsilon}(\omega)=\bar{\epsilon}_1(\omega)+i\bar{\epsilon}_2(\omega)$ given by Eq. (2) we derive the energy-loss function $\mathrm{Im}[-1/\bar{\epsilon}(\omega)]$ which is compared with the EELS spectra. The energy-loss function has poles at $\epsilon_{\rm He}+2\epsilon+2f(\epsilon_{\rm He}-\epsilon)=0$ and yields the excitation energy of the Al volume plasmon, the He $1S$-$2P$ transition,[23] and the BSP dipole mode of the Al/He-bubble system.

With a density-independent atomic electronic polarizability of He ($\alpha_0=0.205$ Å^3, that of liquid He at 4 K)[24] the calculated excitation energy $\hbar\omega_{l=1}(C_{\rm He})$ is shown in Fig. 2. For $f\ll 1$, i.e., $\epsilon_{\rm He}+2\epsilon\gg f(\epsilon_{\rm He}-\epsilon)$ (dashed line), we obtain Natta's result for an isolated bubble, that $\hbar\omega_{l=1}$ increases with increasing $C_{\rm He}$. From experiment ΔE decreases with $C_{\rm He}$ (upper curve in Fig. 2) and with use of Eq. (1) increasing $C_{\rm He}$ means decreasing density n. Accounting for finite He content by using the filling factor given in Eq. (3), we obtain the result shown by the dash-dotted line. The model now describes the experimentally observed decrease of $\hbar\omega_{l=1}$ with increasing $C_{\rm He}$. But still the slope deviates from the experimental one for the low He concentrations and also the curvature is at variance with the experiment. The following effects may be responsible for the discrepancy:

(1) The bubbles in our Al-He system might not be arranged on a cubic lattice and hence the MG model might not be applicable. This is examined by the extended theory of Persson and Liebsch,[25] who go beyond MG by including the dipole-dipole coupling between randomly distributed particles. The results show that random bubble distribution has negligible influence on the excitation energy of the BSP dipole mode but strongly affects the linewidth, giving about twice the experimental value. This result is in agreement with observed superstructure reflections due to bubble lattices.[14] Thus on this point the MG model is applicable.

(2) The excitation energy $\hbar\omega_{l=1}$ depends on the bubble size (spatial dispersion). This has been discussed by Aers, Paranjape, and Boardman,[8] who found that for small bubble radii (in our case up to about 10 Å) the BSP dipole mode is shifted to higher energies. For larger bubble radii this influence can be neglected. Thus, spatial dispersion should affect $\hbar\omega_{l=1}$ at low He concentrations (small bubble radii) and should be quantitatively considered in an extended calculation.

(3) The atomic electronic polarizability α_0 of He might depend on the He density. Although high-pressure data of α_0 are rather scarce this assumption is supported by two observations:
(i) From the low-density measurements of He by Vidal and Lallemand[26] α_0 is found nearly constant up to 0.05 Å^{-3} ($\alpha_0\simeq 0.205$ Å^3), but between 0.05 and 0.06 Å^{-3} a small decrease is observed.
(ii) For the explanation of the change of the relative refractive index of He at the melting point around 300 K Loubeyre *et al.*[27] arrive at an estimate of $\alpha_0\simeq 0.1$ Å^3 at $n=0.138$ Å^{-3}.

Using this extrapolation, we approximate $\alpha_0(n)$ by a linear dependence between $n=0.06$ and 0.138

Å^{-3}; $\alpha_0 = 0.286 - 1.348n$ (n in inverse cubic angstroms). Recalculation of $\hbar\omega_{l=1}(C_{\text{He}})$ by Eq. (2) with this estimate results in the solid line in Fig. 2. The agreement with the experiment is obviously improved.

In conclusion, we have shown that high densities of He bubbles in Al can be used to study collective excitations on cavity surfaces. Our experimental results are reasonably described by the Maxwell-Garnett effective-medium theory including the density dependence of ϵ_{He} in the bubbles and a density-dependent atomic polarizability of He. One should realize, however, that the density gradient of α_0, $\partial\alpha_0/\partial n = -1.35$, is much larger than the value given in Ref. 26, for the density smaller by a factor of 2. This would imply a strong two-atom effect in the intermolecular potential of superdense He. We are well aware that the conclusion to this extent is speculative in that deviations between theory and experiment concerning the curvature of $\hbar\omega_{l=1}(C_{\text{He}})$ still remain, possibly due to additional interactions between the bubbles. This should stimulate further theoretical treatments.

We thank H. L. Bay (Institut für Plasmaphysik, Kernforschungsanlage, Jülich), W. Jäger, and F. P. Johnen for experimental assistance and M. Campagna and W. Schmatz for supporting this work.

[1]M. Natta, Solid State Commun. 7, 823 (1969).

[2]A. A. Lucas, Phys. Rev. B 7, 3527 (1973).

[3]A. A. Lucas, A. Ronveaux, M. Schmeits, and F. Delanaye, Phys. Rev. B 12, 5372 (1975).

[4]G. Mukhopadhyay and S. Ludqvist, Solid State Commun. 17, 949 (1975).

[5]J. C. Ashley and T. L. Ferrell, Phys. Rev. B 14, 3277 (1976).

[6]K. Ohtaka, Phys. Lett. 63A, 298 (1977).

[7]V. V. Maksimenko, A. J. Simenev, and A. A. Lushnikov, Phys. Status Solidi (b) 82, 685 (1977).

[8]A. C. Aers, B. V. Paranjape, and A. D. Boardman, J. Phys. Chem. Solids 40, 319 (1979).

[9]K. Ohtaka, H. Miyazaki, and A. A. Lucas, Phys. Rev. B 21, 467 (1980).

[10]M. Schmeits, J. Phys. C 14, 1203 (1981).

[11]P. Henoc and L. Henry, J. Phys. (Paris), Colloq. 31, C1-55 (1970).

[12]R. Manzke and M. Campagna, Solid State Commun. 39, 313 (1981).

[13]J. C. Rife, S. E. Donnelly, A. A. Lucas, J. M. Gilles, and J. J. Ritsko, Phys. Rev. Lett. 46, 1220 (1981).

[14]W. Jäger, R. Manzke, H. Trinkaus, G. Creclius, R. Zeller, J. Fink, and H. L. Bay, J. Nucl. Mater. 111 + 112, 674 (1982).

[15]R. Manzke, W. Jäger, H. Trinkaus, G. Crecelius, R. Zeller, and J. Fink, Solid State Commun. 44, 481 (1982).

[16]R. Manzke, Kernforschungsanlage Jülich Report No. 1814, 1982 (unpublished).

[17]I. C. Maxwell-Garnett, Phil. Trans. Roy. Soc. London 203, 385 (1904), and 205, 237 (1906).

[18]A. S. Barker, Jr., Phys. Rev. 7, 2507 (1973).

[19]C. G. Granquist and O. Hundri, Phys. Rev. B 16, 3513 (1977).

[20]K. Ohtaka and A. A. Lucas, Phys. Rev. B 18, 4643 (1978).

[21]The damping is given by the experimentally derived linewidth, but can be neglected for the present evaluation.

[22]W. C. Martin, J. Res. Nat. Bur. Stand. 64, 3513 (1977).

[23]The effective-medium theory (MG model) does not quantitatively explain the large shifts of the He $1S-2P$ transition energy for the present high He densities. The dominating mechanism for the He line shift is the strong Pauli repulsion which is discussed in detail by A. A. Lucas, J. P. Vigneron, S. E. Donnelly, and J. C. Rife, Phys. Rev. B (to be published).

[24]A. A. Maryott and F. Buckley, *Table of Dielectric Constants and Electric Dipole Movements of Substances in the Gaseous State*, U.S. National Bureau of Standards Circular No. 537 (U.S. GPO, Washington, D.C., 1953), p. 29.

[25]B. N. J. Person and A. Liebsch, private communication. The model is described by B. N. J. Person and A. Liebsch in Solid State Commun. 44, 1637 (1982).

[26]D. Vidal and M. Lallemand, J. Chim. Phys. 64, 4293 (1976).

[27]P. Loubeyre, J. M. Besson, J. P. Pinceaux, and J. P. Hansen, Phys. Rev. Lett. 49, 1172 (1982).