

Raman Scattering by Bulk Phonons in Microcrystalline Silver and Copper via Electronic Surface Excitations

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In Raman scattering from cryocondensed metal films one observes the bulk acoustic phonons. This is not caused by the laser field which penetrates the metal, but via the scattering of optically excited intrasurface band electron hole pairs by the phonons. Phonons with wave vector \mathbf{Q} contribute to the Raman signal according to the scattering probability $S(\mathbf{q})$ of the image states by surface roughness, where \mathbf{q} is the projection of \mathbf{Q} onto the low index facets having occupied electronic surface states, in the present case mainly of (111) orientation. [S0031-9007(97)04865-5]

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Information on bulk phonons (P_s) in metals throughout the Brillouin zone [1] so far has mainly been obtained by neutron scattering. Surface P_s of metals, especially the Rayleigh P_s , has been investigated by electron energy loss spectroscopy [2] and by inelastic He scattering [3]. Inelastic x-ray scattering has been used in the case of vanadium [4]. Raman scattering (RS) of hexagonal mono-elemental metals like zinc [5] and beryllium [6] yields a weak intensity from the zone center bulk optical P_s . Here we show that RS at clean rough noble metal surfaces is sensitive to the acoustic P_s and propose RS at stepped surfaces of metals with filled electronic surface states (SSs) as a relatively simple method to gain face specific access to the dispersion of the acoustic P_s . It is the first time that surface projected bulk P densities are introduced and electron- P interaction of electrons in SSs is discussed and demonstrated.

The Raman spectra of cryocondensed silver films grown on a smooth substrate at low temperature in ultra high vacuum show broad, but clearly resolvable, low frequency bands at about 65, 110, and 170 cm^{-1} [7], in coincidence with critical points in the P band structure of bulk silver [8], originally assigned to bulk disorder induced light scattering (BDIRS) [6]. In contrast, Roy and Furtak [9] assigned these bands, also observed at roughened silver electrodes, to tetrahedral cationic Ag_4 surface clusters, representing the sites of maximum enhancement of the Raman intensity of adsorbed molecules.

Silver and copper films of 150 nm thickness were evaporated onto a polished copper substrate at 40 K and, respectively, 50 K within UHV. Figures 1 and 2 show the low frequency Stokes and anti-Stokes spectra of silver and the Stokes spectra of copper films annealed at increasing temperatures recorded with a triple monochromator. Since elastic light scattering is maximal after annealing to 350 K [11] the contribution by erroneous stray light is indeed limited to the range $\pm 25 \text{ cm}^{-1}$ in all spectra. Two observations make the assignment to tetrahedral

clusters unlikely: The bands are not altered in shape or in spectral position as the films are heavily reconstructed during annealing (Figs. 1 and 2) or exposure to oxygen (Fig. 3), whereas an Ag-O stretch band at 340 cm^{-1} appears, see Fig. 25 in [12]. It is highly unlikely that the number of Ag_4 clusters even increases during reconstruction. Oxygen does not chemisorb at the smooth (111) facet planes of silver at 40 K, but only adsorbs dissociatively at "surface defects" [13]. If a major fraction of the defects has Ag_4 structure, one has to assume that oxygen attaches to the cluster sites and the frequencies are shifted.

The quenching of the Raman intensity of bulk P_s indicates a surface sensitive mechanism of excitation,

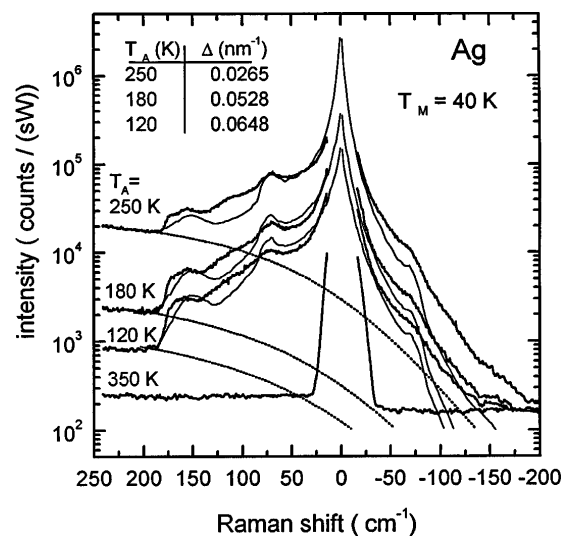


FIG. 1. Thick solid lines are low frequency Raman spectra (laser wavelength $\lambda_L = 514.5 \text{ nm}$, 0.1 W) of a silver film cryocondensed at 40 K, subsequently annealed at the indicated temperatures T_A , for about 120 sec, recorded at $T_M = 40 \text{ K}$. Theoretical spectra as sum (thin solid lines) of the contribution of bulk P_s projected on (111) [Eq. (3) and Ref. [10]] and the intra-Shockley surface band transitions [Eq. (4)], dotted line.

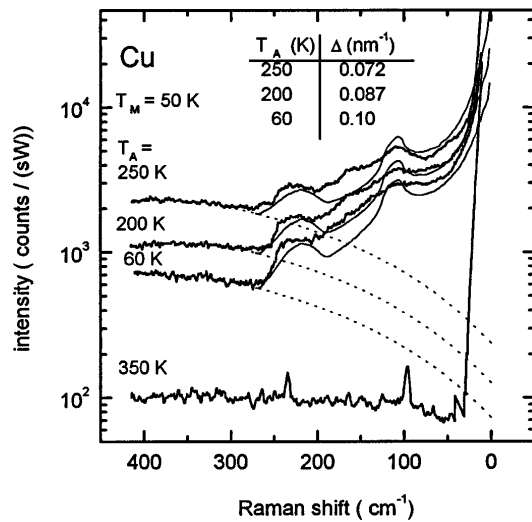


FIG. 2. Like Fig. 1, but copper film, $\lambda_L = 647.1$ nm, 0.2 W.

because the decrease of the local macroscopic field within the metal should be connected with a change of the optical absorption. However, the latter effect is not observed [14]. Apparently BDIRS by P_s within the penetration depth of visible light is too weak because the local macroscopic field factor of RS below the surface is smaller by about a factor of $\epsilon(\omega_L)^{-4}$ compared to sites outside the so-called image plane [15]. In the following, we propose a mechanism involving virtual transitions between electronic SSs.

Most likely, the surface of a cryocondensed and partly annealed film consists of small facets of (111), (110), and (100) orientations, various steps, kinks, and other one- and zero-dimensional defects related to grain boundaries and dislocations. Electronic SSs, well known from large

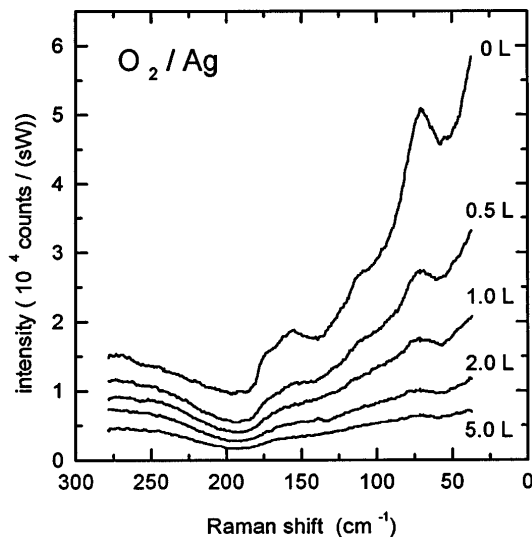


FIG. 3. Low frequency Raman spectra of a silver film annealed at 250 K and exposed to increasing doses of oxygen at 40 K.

single crystal surfaces [16,17], still do exist on small facets, for instance the Shockley (s/p -derived crystal induced) SS at Au(111) was observed spatially confined on terraces with widths in the range of 3 to 6 nm and islands of 4.5 nm diameter [18] and the first image state on Cu(100) with step spacings of 1 nm [19]. The Shockley states may penetrate several lattice constants into the bulk, for instance 2.8 nm at Ag(111) [20]. An electron in this state therefore will scatter not only from surface P_s but also from bulk P_s .

The scattering mechanism is modeled as a fourth order process, involving p -polarized [21] photon annihilation by electronic excitations from the occupied part of the Shockley SS band (S_2 in Fig. 4) to image states (S_1 in Fig. 4), photon creation by electronic transition from S_1 to the unfilled part of S_2 scattering within the S_1 band by surface roughness, and scattering within S_2 by P_s . Also, the scattering within S_2 by surface roughness and within S_1 by P_s will contribute. The resonant process among the 24 differently time ordered processes is schematically given in Fig. 4. An alternative or additional process may involve the electronic transition between the Shockley state and the bulk states above L_1 ; see Fig. 4 and [23].

With the laser wavelength of 514.5 nm one is far out of resonance with the transition between S_2 and S_1 at 318 nm [24] or the bulk states above L_1 . Out of resonance, in the case of RS of vibrations of molecules and bulk crystals, one usually uses the polarizability theory of RS of G. Placzek, see [25], with the assumption of homogeneous laser and Raman fields (frequency ω_L) and at

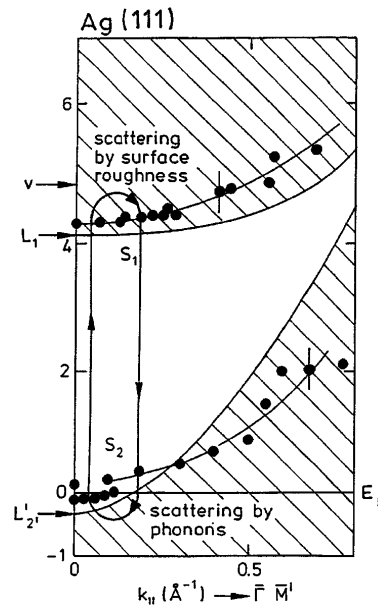


FIG. 4. See text. Hatched area: Bulk electronic band structure projected onto Ag(111). The experimental data of the lowest image state S_1 and the Shockley state S_2 are from Ref. [22]. According to two-photon photoemission and SHG S_1 is found 3.84 eV above S_2 at $k = 0$ [24]. V is the vacuum level.

every site the same derivative of the atomic polarizability with respect to displacement from the equilibrium conditions. This is not possible in our case, because the nonlocal electromagnetic fields are highly inhomogeneous near the surface and the electronic SSs are localized near the surface. Nevertheless, one may define an electronic surface susceptibility χ modulated by lattice vibrations with normal coordinates ξ [26]. Analogous to first order Raman scattering (s: Stokes, as: anti-Stokes) by Ps in crystals (frequency ω_{ph}) we derive for the first order RS at crystalline surfaces the differential Stokes and anti-Stokes power scattering cross sections (1):

$$\frac{d\sigma}{d\Omega} \begin{Bmatrix} s \\ as \end{Bmatrix} = \frac{\omega \begin{Bmatrix} s \\ as \end{Bmatrix}^4}{(4\pi)^2 c^4} F \left| \mathbf{e} \begin{Bmatrix} s \\ as \end{Bmatrix} \frac{d\chi}{d\xi} \mathbf{e}_L \right|^2 \times \frac{\hbar}{2\omega_{\text{ph}}(\xi)} \begin{Bmatrix} n(\omega_{\text{ph}}(\xi)) + 1 \\ n(\omega_{\text{ph}}(\xi)) \end{Bmatrix}. \quad (1)$$

Here \mathbf{e}_s , \mathbf{e}_{as} , and \mathbf{e}_L are the macroscopic Stokes, anti-Stokes, and laser fields above the illuminated surface area F , by the choice of the definition of the surface susceptibility and $n(\omega_{\text{ph}}(\xi))$ is the Bose-Einstein factor. At a smooth surface $\mathbf{k}_s = \mathbf{k}_L - \mathbf{q}$, and $\mathbf{k}_{as} = \mathbf{k}_L + \mathbf{q}$, where the \mathbf{k} and \mathbf{q} vectors are two-dimensional projections of the wave vectors of the laser, Stokes, and anti-Stokes fields and of the wave vector \mathbf{Q} of the bulk lattice vibrations onto the surface. At a smooth surface \mathbf{q} will be very small with respect to the extension of the surface Brillouin zone. However, surface roughness allows for elastic scattering by a two-dimensional vector \mathbf{k}_r . Then, RS becomes possible for Ps with wave vector $\mathbf{q} = -\mathbf{k}_r$. In the following we assume that the cross sections (1) may be integrated over the range of \mathbf{q} for which surface roughness components with $\mathbf{k}_r = \mathbf{q}$ are present. Further we assume a constant tensor $\frac{d\chi}{d\xi}$ for all Ps . We consider only bulk Ps , the relation $\omega_{\text{ph}}(\mathbf{Q})$ for wave vectors \mathbf{Q} throughout the bulk Brillouin zone is obtained by a Born-von Karmann fit [27] to the experimental P dispersion along high symmetry directions (Ref. [8]). The scattering probability of the image state by surface roughness with momentum transfer $\hbar\mathbf{k}_r$ is modeled by a Lorentzian distribution

$$S(\mathbf{k}_r) = \frac{2\Delta}{\pi} \frac{1}{\Delta^2 + \mathbf{k}_r^2}. \quad (2)$$

Integration of (1) weighted by (2) yields the Stokes and anti-Stokes spectra (3), with C_1 being a constant.

$$J_{\text{ph}} \begin{Bmatrix} s \\ as \end{Bmatrix} = C_1 \begin{Bmatrix} n(\omega_{\text{ph}}(\xi)) + 1 \\ n(\omega_{\text{ph}}(\xi)) \end{Bmatrix} \frac{1}{3N\omega} \times \sum_{\mathbf{Q},j} S(\mathbf{q}) \delta(\omega - \omega_{\text{ph}}(\mathbf{Q}, j)), \quad (3)$$

where the index j runs over the three acoustical branches. Using N and Q in the Gilat-Raubenheimer method [28], the projection of the bulk P structure on the three low

index faces yields significant and individual structures, see Fig. 5. Though BDIRS has been ruled out above, we give its expected shape in Fig. 5, which does not resemble the experimental spectra in Fig. 1. To the Raman spectrum of the Ps projected on (111) we add the electronic Raman spectra of the intra-Shockley-band transitions at (111) facets, as given by (4)

$$J_{\text{eh,sh}}(\omega) = C_2 \int f(\varepsilon_{\text{sh}}(\mathbf{k}_{\text{sh}})) S(\mathbf{k}_r) \times [1 - f(\varepsilon_{\text{sh}}(\mathbf{k}_{\text{sh}} + \mathbf{k}_r))] \times \delta(\omega - \varepsilon_{\text{sh}}(\mathbf{k}_{\text{sh}} + \mathbf{k}_r) + \varepsilon_{\text{sh}}(\mathbf{k}_{\text{sh}})) \times d\mathbf{k}_{\text{sh}} d\mathbf{k}_r, \quad (4)$$

where ω is taken positive on the Stokes side and negative on the anti-Stokes side and $f(\omega)$ is the Fermi-Dirac distribution. The quadratic dispersion $\varepsilon_{\text{sh}}(k_{\text{sh}})$ of the Shockley band was modeled with the experimental data [29] at 65 K $\varepsilon_{\text{sh}}(k_{\text{sh}} = 0) - E_F = -60$ meV and $m_{\text{eff}}/m = 0.43$.

We neglect the intrasurface band transitions at (110) and (100) facets because we expect that (111) facets are more abundant than the (110) facets, particularly when annealing to a temperature of 250 K and because the intensities will depend on the number n of occupied SSs per unit area in the sense $n(111) \approx n(110) \gg n(100)$. For Cu quantitative data are compiled in [30]. By assuming two-dimensional isotropic dispersion of the occupied SSs near the X point of the (100)-, the Y point of the (110)-, and the Γ point of the (111)-surface Brillouin zone, the number n of electrons in the SSs per surface atom is calculated as $n(100) = 0.010$; $n(110) = 0.0407$; $n(111) = 0.0424$. A detailed calculation in the sense

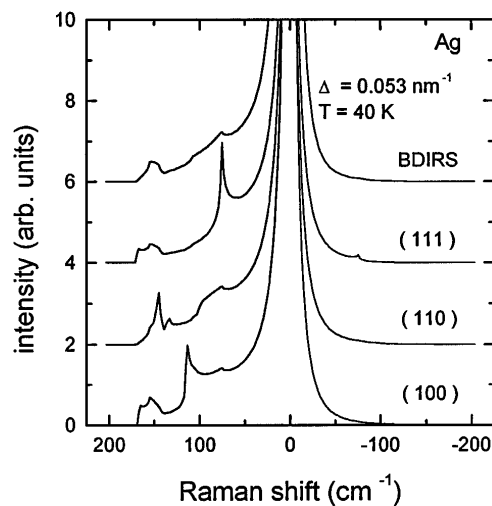


FIG. 5. Theoretical RS spectra of the bulk Ps of silver (data of Kamitakahara and Brockhouse [8]), for projections on the three low index faces and for BDIRS [bulk disorder analogue to Eq. (2)]. Spectra have been displaced vertically from the zero position at -200 cm^{-1} .

of Eq. (4) for copper yields a ratio of the intensities of intrasurface band transitions at (111):(110):(100) of 1:0.33:0.03. On Ag(110) one has to expect a resonant contribution at a laser photon energy of 1.75 eV because of transitions between an occupied and an unoccupied crystal induced SS, as observed by second harmonic generation [31]. At the laser photon energy of 2.41 eV one is well outside of this resonance.

The P signal, which is 1 to 2 orders of magnitude stronger than the background, can be well fitted by four parameters (three values of Δ given in Figs. 1 and 2 and one common factor C_1/C_2). For the background we had to choose three values of C_2 increasing with T_A , which may reflect $\varepsilon_{sh}(\mathbf{k}_{sh} = 0)$ decreasing with increasing facet size [32]. Thus, there are altogether seven fitting parameters. The decrease of the fitting parameter Δ with increasing T , see Figs. 1 and 2, reflects the eventual smoothening of the film. The small deviations from the experimental spectra at about 166 and 112 cm^{-1} (see Fig. 1) is assigned to (110) facets. The absence of a discrete structure at about 115 cm^{-1} means that (100) facets do not contribute, according to $n(111) \approx n(110) \gg n(100)$. The Rayleigh P_s of Ag(111) [33] at 68.5 and 73.4 cm^{-1} at the M and K point of the (111) surface Brillouin zone probably contribute to the structure at 68 cm^{-1} in Fig. 1, but are not separated from the bulk P signal due to the small differences in energy of bulk and Rayleigh P_s at the M point. There is no peak at very low frequencies of 10–20 cm^{-1} , in agreement with experiments described in [34].

The effect of quenching is assigned to a depletion of electrons in the SSs by atomic oxygen adsorbed at sites of atomic scale roughness and the transfer of electron density at E_F into the $O2p$ orbitals, 2.9 eV below E_F [35]. Given the density n of electrons in SSs estimated above, an O^{x-} atom at the surface depletes an area of x/n surface unit cells. The optical electron transfer transition from the $O2p$ orbital to the depleted SS yields the surface enhanced RS signal of the O-metal vibration.

A detailed comparison with the surface structure will be possible only when using single crystalline vicinal faces.

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