# Quantum Size Effects in Excitations of Potassium Clusters

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The electronic excitations of potassium clusters embedded in a MgO matrix have been investigated as a function of cluster size and momentum transfer by means of electron-energy-loss spectroscopy. The experimental results show deviations from predictions of classical electrodynamics but they are in qualitative agreement with a calculation for excitations of a jellium sphere made with use of the time-dependent local-density approximation.

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The electronic structure of small metal particles has been the subject of a large number of recent theoretical and experimental studies.[1] Deviations from the bulk electronic structure are expected from the influence of the surface and from quantum size effects, i.e., the transition from a continuous conduction band into discrete levels. Experimentally, the electronic structure of small particles can be studied by measuring excitations such as single-particle and collective excitations. Classically, in the framework of an electrodynamical theory,[2] there exist for metallic spheres besides the volume plasmon with energy $\hbar\omega_p$, also a series of multipolar surface plasmons with energies

$$\hbar\omega_l = \hbar\omega_p\{1+[(l+1)/l]\epsilon\}^{-1/2},$$

where $l$ is the angular momentum quantum number and $\epsilon$ reflects the influence of the background dielectric constant of the host material which partially screens the surface oscillations. Theoretical calculations for *small* particles predict deviations of the microscopic response properties from that predicted by classical electrodynamics.[3] Experimentally, there are various electron-energy-loss spectroscopy (EELS) studies[4-7] on the long-wavelength limit of the plasmon spectra of metal clusters which are related to the dipolar ($l=1$) response.

In this paper, we report for the first time on wavelength-dependent EELS studies of the dynamical response of small metallic particles. Potassium particles in a MgO matrix have been used since K is a simple metal and MgO offers a sufficiently large energy gap of almost 8 eV, needed for the observation of the valence electron excitations of the K cluster. Regarding the electronic response, strong deviations were observed compared to the results predicted by electrodynamical calculations. In particular, the individual surface modes for $l \geq 2$ are strongly blue shifted and by superposition they form a band of excitations with a strong dispersion in momentum transfer. At higher momentum transfer, the collective modes are more and more coupled to single-particle excitations, forming a broad continuum of excitations between the classical dipole mode and the volume plasmon. The results are compared with recent calculations[3] on the dynamic response of a small jellium sphere using the time-dependent local-density approximation.

Epitaxially grown MgO films with thicknesses of less than 1000 Å were produced by evaporation of MgO onto a single crystalline LiF film of about 200 Å thickness. The LiF films were grown in a preceding evaporation step using freshly cleaved NaCl single crystals with an (100) orientation of the surface. A nearly homogeneous distribution of K atoms in the MgO host matrix was realized by implanting a dose of $1.2\times10^{16}$ $K^+/cm^2$ with an energy of 80 keV at liquid-nitrogen temperature. The total amount of implanted K was about 1 at.% in accordance with the amount of trapped atoms determined by Rutherford backscattering measurements. Extensive electron microscopy studies on alkali metals in MgO have proven that annealing of the implanted films results in reasonably narrow size distributions of spherically shaped clusters, the mean size of which is strongly dependent on annealing temperature and only weakly dependent on annealing time.[8] We chose an annealing time of 40 min and three different temperatures, 800, 700, and 650 °C to obtain samples with a mean diameter of about 80, 40, and 20 Å, respectively. The diameters of the spheres were estimated from the momentum dependence of the volume plasmon intensity (see below) and the given values have a large error, in particular for the smaller spheres. For annealing at 600°C no precipitation could be observed. Transmission EELS measurements at room temperature were performed with a high-resolution 170-keV spectrometer.[9] The energy and momentum resolutions were chosen to be 0.16 eV and 0.04 $Å^{-1}$, respectively.

 

Figure 1 shows energy-loss spectra taken at momentum transfer $q = 0.2$ Å$^{-1}$ for *MgO*K samples annealed at three different temperatures. The spectra are shown in the energy range between the primary beam (zero energy loss) and the MgO gap edge located at 7.7 eV. All the curves are normalized to the height of the gap edge, which falls off approximately proportional to $q^{-2}$. In the uppermost spectrum two dominant loss maxima occur at 1.7 and 3.9 eV, which can be attributed to collective excitations of the clusters. The latter maximum stems from the well-known volume plasmon excitation. The intensity at about 6 eV is due to multiple-scattering effects.

The slight increase in volume plasmon energy compared to 3.8 eV in bulk is an effect of the surface tension which compresses the clusters. A pressure of some $10^4$ bars can be deduced from the corresponding shift of the diffraction pattern and from the enhancement of the melting point of potassium.[10] The loss maximum at 1.7 eV is caused by a superposition of multipolar surface modes. To calculate the energies of the surface plasmon modes in the classical limit, we used for the MgO matrix the static dielectric constant $\epsilon_{MgO} = 3$, which is a crude approximation, especially at higher momentum transfer. Nevertheless, the calculated energy of 1.4 eV for the dominant dipolar ($l = 1$) mode is very close to the experimental loss maximum at 1.7 eV. The highest modes ($l = \infty$) should appear in this classical approximation at 1.9 eV. The range of these classical excitations is indicated by the vertical lines.

As shown in the lower curves of Fig. 1, the volume plasmon intensity is strongly reduced with decreasing diameter of the K clusters. In addition, new loss maxima appear in the energy range 2 to 3 eV, i.e., beyond the classical limit $l = \infty$ for spherical shaped spheres.

In Fig. 2 we show spectra as a function of momentum transfer $q$ for a *MgO*K sample annealed at 700 °C. Again all the spectra are normalized to the intensity at the gap edge of MgO. At low momentum transfer, the volume plasmon intensity is small and almost independent of $q$. At higher momentum transfer the intensity is higher and decreases with $q^{-2}$. Finally, for large $q$ approaching the critical wave vector $q_c \approx 0.75$ Å$^{-1}$ the plasmon decays into electron-hole excitations as in bulk K metal. Also the volume plasmon dispersion is very close to that in bulk material. The anomalous intensity variation of the volume plasmon (not proportional to $q^{-2}$) for $qR \lesssim 1$, where $R$ is the sphere radius, has already been predicted in electrodynamical calculations.[11,12] As a consequence of a sum rule, for $qR < 1$ the surface excitations are strongly enhanced at the expense of the volume plasmon excitations. This is in agreement with our spectra shown in Fig. 2. The intensity variation of the volume plasmon has been used to estimate the mean radius of the K cluster.

The volume plasmon half-width is considerably enhanced in comparison to its bulk value, as has already been observed in earlier EELS and optical investigations.[4,5,13,14] Whereas in bulk we measured a half-width of 0.24 eV (Ref. 15) in the long-wavelength limit, in the case of clusters the half-width is higher by a factor of 2.5. The investigation of the $q$ dependence of this effect

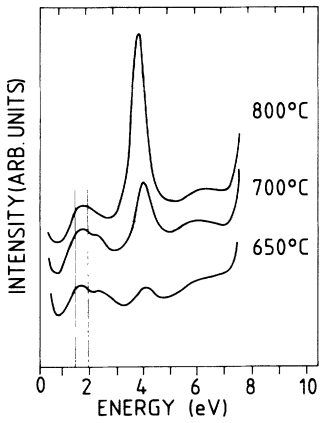


FIG. 1. Energy-loss spectra of K clusters embedded in MgO, taken at $q = 0.2$ Å$^{-1}$. The three samples were produced by annealing the same implanted specimen up to the given temperature. The vertical lines indicate the classical energy range of surface plasmon frequencies on spherical particles.

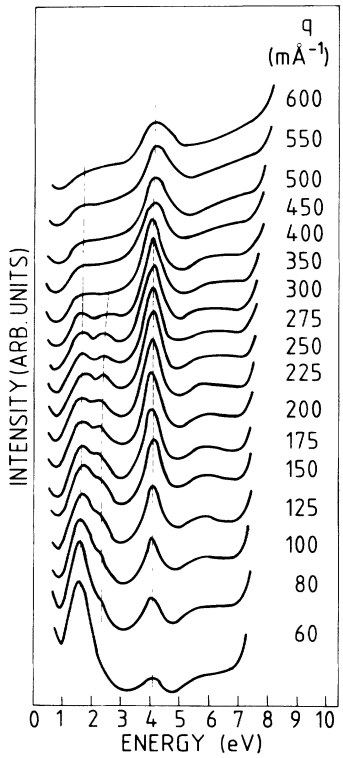


FIG. 2. Energy-loss spectra of K clusters embedded in MgO, annealed to 700 °C for 40 min. The spectra were taken at the momentum transfers indicated. The dashed lines mark the slight positive dispersion of the nonclassical excitations.

yields that at higher $q$ the half-widths of the plasmons in bulk and clusters get closer together. This implies that the main part of the plasmon broadening at low $q$ is due to a decay into surface excitations.

According to the above mentioned classical calculations, at low $q$ the surface modes have dominantly dipolar character ($l=1$) and the loss maximum at $\sim 1.7$ eV is close to the classical dipole value. With increasing momentum transfer, the dipole mode decays, in agreement with electrodynamical calculations. However, while for higher $q$ classically higher modes should appear for $E \leq \hbar\omega_{l=\infty} \lesssim 1.9$ eV, there appears a new excitation above this energy. This mode is more and more pronounced with increasing $q$ until it broadens and smears out at about $q=0.4$ Å$^{-1}$. While the dipole mode shows almost no dispersion, the new mode has a considerably larger dispersion than the volume plasmon. We emphasize that similar results were obtained for the sample with the smallest K clusters and also for Na and Rb clusters in MgO.

In order to obtain more information on the nature of these new excitations, we compare our results with previous theoretical calculations[3] of the dynamical response of a jellium sphere in vacuum composed of 92 atoms using the time-dependent local-density approximation. In Fig. 3 we present calculated electron-energy-loss spectra for the momentum transfers $q=0.2$, 0.4, and 0.6 Å$^{-1}$. The energy scale is normalized to the energy of the volume plasmon. The spectra have been folded with a Gaussian function of 0.2-eV half-width, corresponding to the achieved experimental resolution. At low momentum transfer ($q=0.2$ Å$^{-1}$) the theory yields a loss spectrum dominated by the intense $l=1$ dipole surface mode at $E/E_p \approx 0.5$. This value is smaller than the value calculated in the classical limit ($E/E_p=0.58$) because the electron density of the cluster leaks out beyond the edge of the jellium sphere. Thus, the mean electron density is lower than in bulk causing a lower frequency for collective excitations. In our case, however, the electronic density is prohibited to leak out because of the repelling electrons in the MgO matrix. Therefore, the red shift should not be observed. The volume plasmon located at $E/E_p=1.0$ is strongly suppressed. Already at $q=0.2$ Å$^{-1}$ there is some loss of intensity in the classically forbidden energy range between the classical $l=\infty$ surface mode ($E/E_p \sim 0.7$) and the volume plasmon. With increasing momentum transfer the intensity of the volume plasmon increases, whereas the intensity of the dipole mode is rapidly reduced. At $q=0.4$ Å$^{-1}$ another surface mode, the quadrupole mode, appears. At even higher momentum transfer ($q=0.6$ Å$^{-1}$) the intensity of the quadrupole mode is reduced whereas one finds higher modes extending beyond the classical $l=\infty$ limit (located at $E/E_p=0.7$) up to the volume plasmon. One may speak of a dispersion in the sense that not the individual $l$ modes but their superposition forms a peak which moves to higher energies with increasing $q$. The intensity of the nonclassical excitations in the low-energy region has further increased. What is the nature of all these excitations? By examination of the calculated complex dynamic polarizability it can be shown that only the volume plasmon and the dipole mode are of truly collective character. The excitations below the dipole mode are dominantly particle-hole excitations as a result of split energy-level systems of the considered cluster. The so-called quadrupole mode already is not of pure collective nature but couples to single-particle-hole excitations. Roughly speaking, the particle-hole character prevails more as the modes disperse beyond the classical $l=\infty$ limit. This evolution reflects that, because the crystal momentum is no longer a good quantum number, all the excitations in a small cluster couple mutually. With reduction of the size of a cluster, surface and volume plasmons as pure transversal and longitudinal excitations are no longer well defined.

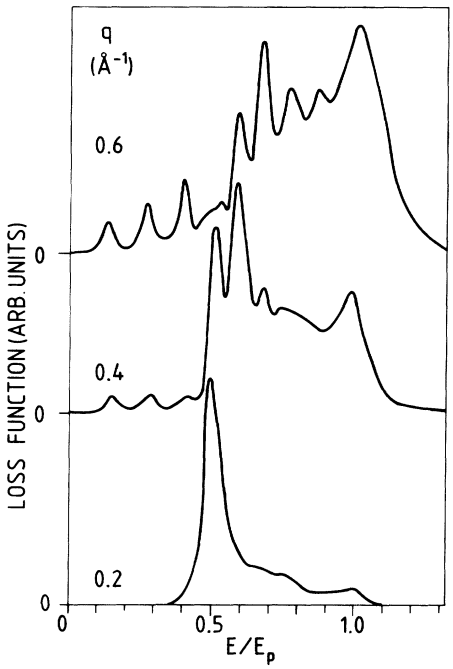


FIG. 3. Jellium model calculations for $r_s/a_0=4$ for the energy-loss spectra of a 92-atom cluster for three different momentum transfers.

A quantitative comparison of the theoretical with the experimental results is not possible since the jellium sphere was considered to be in vacuum and not in MgO, and the electron density was chosen to be close to metallic Na and not K. Nevertheless, there is a remarkable qualitative agreement between the experimental and theoretical results. In small spheres, there is almost no volume plasmon at low $q$. The low-$q$ loss spectrum is dominated by the dipole surface plasmons. At higher momentum transfer the intensity of the dipole mode falls

faster than as $q^{-2}$. Higher multipole modes appear and disappear at higher $q$ thus forming by superposition a new band of excitations which show a strong dispersion in momentum transfer. We emphasize, however, that according to the calculations, the individual multipole modes have *no* dispersion. In the experiment, this is observed for the dipole mode, while the higher modes could not be resolved because of the size distribution of the clusters. The level quantization of the single-particle levels, i.e., quantum size effects, leads to a blue shift because the coupled oscillators are replaced with those of a stiffer force constant. Therefore, excitations appear at higher momentum transfer between the classical $l=\infty$ mode (the planar surface plasmon) and the volume plasmon. The surface-induced coupling of the single-particle excitations and the collective surface excitations leads to a smaller critical wave vector than that of the volume plasmon. This is clearly seen in Fig. 2. Above $q \cong 0.4$ Å$^{-1}$ the size-dependent Landau damping of the collective surface modes is so large that only a broad continuum of single-particle excitations is observed in the energy range between the dipole mode and the volume plasmon.

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