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Evolution of the Collective-Mode Resonance in Small Adsorbed Sodium Clusters

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The optical spectra of small isolated sodium clusters adsorbed on a boron nitride surface have been measured from 3000 to 7500 Å over a range of average cluster size $\langle N \rangle = 10$–300 atoms by change in reflectivity spectroscopy. The spectra are dominated by the dipole resonance of the surface collective mode of the sodium valence electrons, and the resonance frequency shifts from 2.4 eV to near the bulk value of 3.4 eV as cluster size increases. A quantitative comparison of experimental results with the jellium model of sodium clusters is presented.

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Current interest in the physics of metal clusters has concentrated on developing an understanding of the transition of cluster physics from the quantum domain to a state characterized by bulk properties of the metal. The photoabsorption cross section[1] and photoionization threshold[2,3] of alkali-metal clusters in a molecular beam are examples of recent experiments measuring the variation of cluster electronic properties as a function of cluster size ($N < 50$ atoms). Previous measurements of the optical spectra of metal clusters[4] have been obtained for clusters embedded in matrix environments which precluded observing spectra related to an unperturbed cluster charge distribution. In addition, these matrix studies covered a range of larger cluster sizes ($N > 1000$) which obscured quantum size effects.

The Letter reports measurements of the charge in reflectivity spectra induced by sodium microclusters adsorbed on pyrolytic boron nitride (BN) surfaces for a range of average cluster size from $\langle N \rangle = 10$ to 300 atoms per cluster. These spectra extend from 3000 to 7500 Å and exhibit line shapes dominated by the dipolar collective-mode resonance of the valence electrons. This surface-plasma resonance frequency is observed to shift from a lower energy of about 2.4 eV at the smallest adsorption levels to near the bulk limit of 3.4 eV as the cluster size increases. The advantages of applying reflection spectroscopy in these measurements is the large enhancement of the sensitivity to small changes in the reflectivity which occurs when the surface is probed near the BN Brewster angle.

The experimental apparatus was designed to measure the change in reflectivity, $\Delta R/R$, of an atomically clean BN surface during exposure to a flux of sodium atoms. A tunable radiation source was formed by a high-pressure Xe arc at the input to a Spex 3/4m spectrometer, and the output beam was split into a signal beam, which probed an ≈ 2-mm-diam portion of the BN surface exposed to sodium flux, and a reference beam, which probed a surface portion shielded from exposure. The reflected signal and reference beams were detected simultaneously by separate photomultiplier tubes and lock-in amplifiers using a 1-sec time constant, and data were digitized for analysis by 16-bit analog-to-digital converters. The change in reflectivity was determined experimentally from the ratio of detector signals from the reflected reference and signal beams corrected for detector response. The spectrum of $\Delta R/R$ was obtained by averaging over a sample of ratios taken at each wavelength. A minimum detectable change in reflectivity of $\Delta R/R = 0.1\%$ was set by detector shot noise.

The UHV chamber containing the BN sample and sodium oven was maintained at 1×10^{-10} Torr during experiments, while an internal shield at 110 K surrounding the BN sample reduced the water vapor background pressure to $\leq 10^{-12}$ Torr. The sodium source was a Knudsen effusion cell of 0.9-mm aperature diameter specifically designed to avoid contamination at low vapor pressures (10^{-6}–10^{-5} Torr) whose atomic flux was calibrated absolutely using a Re wire Langmuir probe. The surface of pyrolytic BN (Union Carbide) is an array of basal-plane microcrystals of hexagonal structure which exhibit preferential orientation of the *c* axis normal to the planes[5] and have an average basal-plane diameter of ≈ 150 Å. Polished BN samples ($16 \times 16 \times 1.5$ mm^3) were clamped on a molybdenum holder and mounted on the tip of a He cryostat, which allowed the surface to be simultaneously exposed to sodium flux and radiative probe beams. Auger-electron spectroscopy verified a clean surface of near stoichiometric composition. The absolute run to run reproducibility of $\Delta R/R$ within ± 0.02 confirms that heating the BN to 140°C for 1 h after each experimental run was adequate to maintain surface cleanliness and reproduce the optical reflectivity.

Figure 1 displays spectra of the change in reflectivity taken over a range of integrated Na flux from 3.6×10^{13} to 4.8×10^{14} atoms cm^{-2} for probe polarization parallel to the plane of incidence. Spectral scans were recorded after exposing the BN surface at 40 K to a sodium flux of 8.5×10^{10} atoms cm^{-2}sec^{-1} for varying time intervals. For data taken at integrated flux levels of $n \leq 6 \times 10^{14}$ atoms cm^{-2}, the cluster spectrum was a single, unstructured band whose peak amplitude grows linearly with integrated flux characteristic of isolated metal clusters of nearly spherical geometry. The most significant

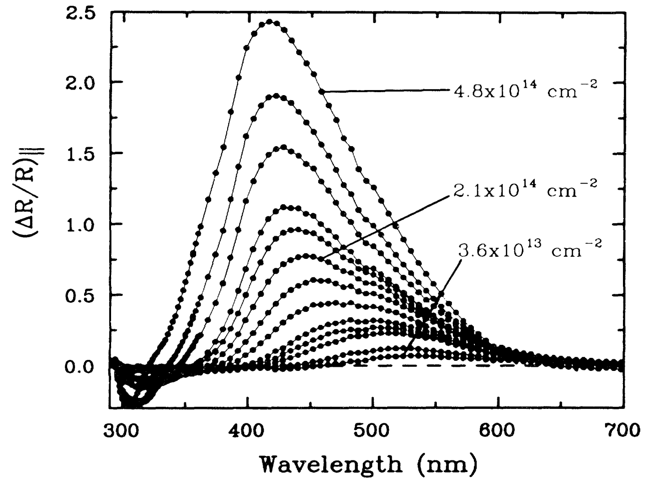

FIG. 1. Spectral scans of reflectivity change vs wavelength for parallel polarization. Several values of total integrated flux (atoms cm $^{-2}$) are indicated.

feature in these spectra is the continuous shift of the peak toward longer wavelengths for decreasing sodium exposures. This frequency shift has been measured for substrate temperatures up to 200 K. The absolute run to run reproducibility of the peak frequency data was within ±0.04 eV. As shown in Fig. 1, the change in reflectivity line shape exhibits amplitude sign reversal at shorter wavelengths as the fixed incident angle approaches the Brewster angle for wavelengths near 300 nm. When the integrated flux exceeds $n > 6\times10^{14}$ atoms cm $^{-2}$ on a substrate at 40 K, a second peak begins to appear in the spectrum near 3200 Å. The amplitude of this peak grows nonlinearly with integrated flux and the peak is suppressed at higher substrate temperatures. Such behavior suggests this secondary peak represents the onset of aspherical distortion or aggregation, which would introduce additional resonances and depend strongly on cluster mobility.

Cluster resonance frequencies were extracted from experimental $\Delta R/R$ spectra as a function of integrated flux by comparing the data with an analytic expression derived for $\Delta R/R$ by extending previous calculations based on dyadic Green's-function methods[6] to formulate E_{sc}, the field scattered in the specular direction by a spatially uniform cluster distribution. The total electric field at the detector resulting from the interference between the reflected incident field, $E_r = R_{\parallel}E_i$, and the scattered field then yields the change in reflectivity for an incident field of amplitude E_i and reflection coefficient $R_{\parallel}$. The expression for $\Delta R/R$ includes a term linear in $|E_{\text{sc}}/R_{\parallel}E_i|$ corresponding to the first Born approximation, and in addition, a term proportional to $|E_{\text{sc}}/R_{\parallel}E_i|^2$ arising from coherent scattering by clusters within an area $\sim\lambda^2$. For an incident angle near the BN Brewster angle, the specular scattered field produced by the Na cluster polarizability can easily become comparable to or even greatly exceed the reflected field from the bare surface. Experiments reported here were performed at an incident angle of 62.5°, for which the BN reflectivity of $R = |R_{\parallel}|^2 \approx 0.15\%$ greatly enhanced the experimental sensitivity to the cluster scattered field and provided the opportunity to measure the evolving cluster physics as the number of atoms slowly increased. This technique is generally applicable to any surface having weak absorption at the probe wavelength.

The polarizability of an adsorbed cluster is derived self-consistently as a function of the isolated cluster polarizability, α_0, which follows from Mie theory for metal spheres. Using the Drude dielectric function to describe the Na metal response, the polarizability for an isolated cluster of N free electrons is

$$\alpha_0 = \frac{e^2N}{m}\frac{1}{\omega_{\text{sp}}^2 - \omega(\omega + i\Gamma)},$$

where ω_{sp} is the surface-plasma frequency which characterizes the collective-mode resonance of the cluster valence electrons, and Γ describes the damping of this mode. This equation for α_0 assumes that the total oscillator strength at the resonance ω_{sp} is accounted for by the surface collective mode. In this case a sum-rule approximation has been derived[7] relating ω_{sp} to the cluster polarizability $\alpha(0)$ given by $\omega_{\text{sp}}^2 = Ne^2/m\alpha(0)$. The polarizability of clusters adsorbed on the BN surface will be anisotropic in the presence of a local field arising from the incident external field and the near field of the surface-induced dipole. Calculation of the polarizability of an adsorbed cluster indicates that the BN surface produces only a small perturbation ($< 2\%$) of the resonance frequency and amplitude of α_0.

In the calculation of $\Delta R/R$, it is assumed that all Na atoms striking the BN surface at 40 K remain on the surface and become incorporated in cluster growth. In addition the spectrum is assumed to be dominated by the cluster parameters ω_{sp} and Γ of the average cluster size $\langle N\rangle$, which is a good approximation when the contribution of inhomogeneous broadening $\Gamma_{\text{inh}} \ll \Gamma$. The effect of a cluster size distribution on the reflectivity change spectrum is then approximated by setting the integrated flux $n = \sigma_0\langle N\rangle$, where σ_0 is the density of clusters having an average cluster size $\langle N\rangle$. As a result, the calculated $\Delta R/R$ depends only on ω_{sp}, Γ, and the experimental variable n through the product $\sigma_0\alpha$. Values for ω_{sp} and Γ were determined as a function of the experimental variable n by varying these parameters to fit the peak frequency and peak amplitude, respectively, of each experimental spectrum in Fig. 1. Comparisons of calculated $\Delta R/R$ line shapes with experimental cluster spectra are shown in Fig. 2. The calculated spectra reproduce features of the observed line shapes reasonably well for this level of analysis. Figure 2 indicates the overall trend that as n increases the linewidth of the experimental spectrum becomes increasingly broader than the calcu-

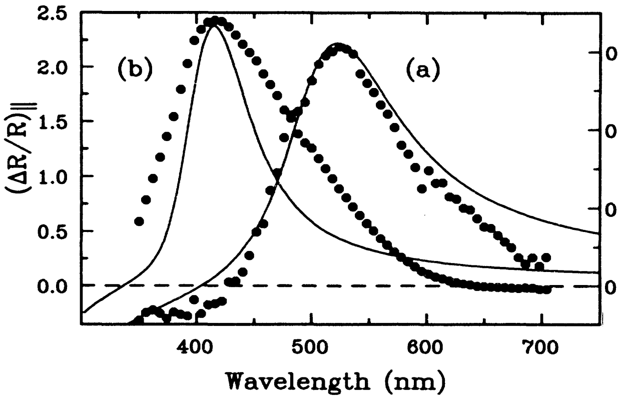

FIG. 2. Comparison of experimental (circles) reflectivity change spectra and calculated (line) spectra for (a) $n=5.1\times10^{13}$ atoms cm^{-2}, $\omega_{\mathrm{sp}}=2.52$ eV, and $\Gamma=0.62$ eV and (b) $n=4.8\times10^{14}$ atoms cm^{-2}, $\omega_{\mathrm{sp}}=3.16$ eV, and $\Gamma=0.59$ eV. [Note different vertical scales (a) on right and (b) on left.]

lated linewidth.

To make contact with current theoretical models of the cluster physics, it is necessary to relate the frequency ω_{sp} and linewidth Γ obtained from the experimental spectra to the average cluster size $\langle N\rangle$. Comparison of the experimental result, ω_{sp} vs n, with the variation of ω_{sp} vs N, obtained independently from measurements of the mean static polarizability[8] via the sum-rule approximation, provides the required relationship between the average cluster size $\langle N\rangle$ and the experimental variable n for adsorbed clusters. To within the accuracy of this analysis, the growth of cluster size $\langle N\rangle$ is found to depend *linearly* on the integrated flux n with an absolute uncertainty in $\langle N\rangle$ estimated to be approximately ±6 atoms. This behavior is characteristic of cluster growth kinetics dominated by the rapid diffusion of atoms adsorbed on a surface having a saturated density of nucleation sites.[9] The cluster density calculated from $\sigma_0=n/\langle N\rangle$ is constant within experimental uncertainty having an average value of $\langle\sigma_0\rangle=(4.3\pm0.7)\times10^{12}$ clusters cm^{-2}. This result for $\langle\sigma_0\rangle$ is consistent with the high density of defect sites which form the perimeter of each BN crystallite and suggests that at low temperature sodium atoms diffuse primarily within the crystallite area prior to attaching to clusters bound at defect sites on the perimeter. This kinetic model is consistent with the results of thermal desorption studies of these clusters which show sodium atoms bound to the BN surface by ≤ 0.2 eV and provide an independent measurement of the cluster density $\langle\sigma_0\rangle$ comparable with the adsorption value.

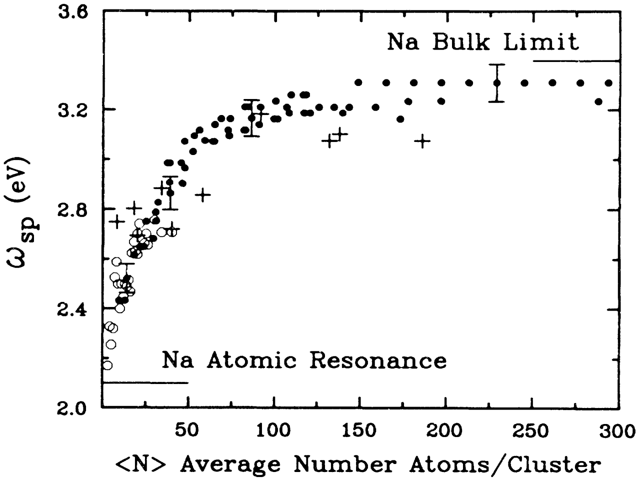

FIG. 3. Cluster resonance frequency vs $\langle N\rangle$ for Na clusters. Frequencies derived from reflectivity change spectra (solid circles) and frequencies calculated via sum rule from static polarizabilities of Ref. 8 (open circles) are compared with theoretical calculations from Ref. 10 (crosses).

The above analysis results in the plot of cluster resonance frequency ω_{sp} vs $\langle N\rangle$ indicated by solid circles in Fig. 3. Cluster resonance frequencies derived from the mean static polarizability by sum rule are indicated in Fig. 3 by open circles. A smooth curve fitted to these sum-rule frequencies was then used to associate each cluster resonance frequency obtained from our measured $\Delta R/R$ spectra with an average cluster size $\langle N\rangle$ for $n\leq2.5\times10^{14}$ atoms cm^{-2}. The average cluster density $\langle\sigma_0\rangle$ is finally used to extrapolate to larger $\langle N\rangle$ for frequencies approaching the bulk limit. The cluster resonance ω_{sp} increases from frequencies above the Na atomic $3s$-$3p$ resonance with a slope determined by the static polarizability data for $\langle N\rangle<40$, and approaches the classical limit, $\omega_p/\sqrt{3}=3.4$ eV, for clusters as small as $\langle N\rangle\approx125$ atoms. For $\langle N\rangle>150$, the frequency ω_{sp} is approximately constant, although the cluster peak amplitude continues to grow linearly with integrated flux. The relative frequency uncertainty of approximately $\pm2\%$ shown in Fig. 3 includes inaccuracy introduced in both determining the peak frequency as well as by the run to run variability. This analysis has assumed that the resonance frequency is not significantly perturbed by cluster-cluster interactions. An estimate of the frequency shift resulting from dipole-dipole interactions[11] among Na clusters separated by $1/\langle\sigma_0\rangle^{1/2}$ indicates an increase of the cluster resonance by $\approx5\%$ for a cluster size $\langle N\rangle=120$, which reinforces this approximation.

Theoretical eigenfrequencies for the surface-plasma mode of Na spheres ($r_s=4$ a.u.) have been calculated recently by Beck[10] in the spherical jellium model and these results are indicated in Fig. 3 by crosses. The general trend of experimental frequencies is in qualitative agreement with theoretical calculations; however, the clear deviation from theoretical results remains to be explained. Although the sum-rule approximation is expected[7] to become less accurate at smaller cluster sizes, the resonance frequencies for $\langle N\rangle\leq50$ display a discrepancy with theory consistent with that observed in measurements of the measurements of the static polarizability.[8] At larger $\langle N \rangle$ values, the resonance frequency can exceed the threshold for single-particle bound-continuum transitions,[10] which may contribute significantly to the experimental peak. Finally, the distribution of adsorbed cluster sizes requires more analysis to evaluate its effect on extracting cluster parameters from the spectral data. Values of Γ obtained from fitting the peak amplitude of $\Delta R/R$ approach theoretical estimates[12] for Landau damping only in the limit of small $\langle N \rangle$ where calculated and experimental line shapes are observed to be in agreement in Fig. 2. Deviation from calculated line shapes occurring for larger cluster sizes can result from inhomogeneous broadening which would increase with $\langle N \rangle$ as the distribution width increases. In addition, as $\langle N \rangle$ increases, the character of the broadening will vary throughout the spectrum line shape as a result of the dependence of ω_{sp} on $\langle N \rangle$.

To summarize, reflectivity change measurements of the spectra of adsorbed Na clusters determines the dependence of the evolving surface-plasma frequency on cluster size. The shift of the cluster resonance to lower frequency arises as the surface charge distribution becomes increasingly diffuse with decreasing cluster size. The range of cluster sizes measured is sufficient to observe the transition of cluster electronic properties to a state characterized by the bulk parameters of metallic sodium. Experiments which attempt to independently measure the cluster size distribution are planned. Measurements of the cluster size dependence of the collective modes of potassium clusters are in progress.

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