

Substrate-induced multipolar resonances in supported free-electron metal spheres

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The optical response of small potassium particles grown on an oxidized silicon substrate has been investigated by surface differential reflectivity spectroscopy. Together with the usual dipolar resonance, an additional resonance is observed in the spectra at larger energy. We assign the origin of this resonance to the multipolar coupling between the potassium particles and the substrate. This is demonstrated by the good agreement found between the experimental data and spectra calculated using a model where this multipolar coupling is included. [S0163-1829(99)11731-4]

The optical properties of metal discontinuous films have received considerable attention during the last 20 years.¹⁻¹¹ Discontinuous films are usually formed at some stages of metal deposition on an insulating substrate, and in some cases they might consist of a collection of supported small metallic particles. The optical properties of discontinuous metal films formed by particles whose size is much smaller than the wavelength of light depend, among other things, on the shape of the particles and their induced mutual interaction in the presence of the substrate. In the dilute limit, the particles interact only with the substrate, which can modify their optical properties significantly in comparison with those of free-standing particles. For example, in the case of a small free-standing metallic sphere, only the Mie dipolar mode can be excited by a long-wavelength applied electric field. But for a sphere supported on a substrate, the field induced on the substrate acts on the sphere. Since this field might not be homogeneous over the volume of the sphere, even if the substrate is flat, multipolar modes higher than the dipole can also be excited, as has been theoretically predicted.^{6,8} In the simplest model this multipolar coupling (MC) is neglected, and the field induced by the substrate is regarded as one coming from the mirror-image dipole. This produces a red-shift in the resonant frequency of the dipolar mode.¹⁰ The mutual interaction among the particles has been treated by regarding the system as a collection of induced dipoles together with their corresponding images. This model was first introduced to interpret differential reflectance experiments on adsorbed monolayers of molecules,⁵ and it has been widely used and refined in the interpretation of optical experiments on both adsorbed molecules¹² and supported discontinuous thin films.^{1-3,13} But the difference in size between adsorbed molecules and supported particles of nanometric dimensions demands different approaches to the optical-

response problem as well as the identification of different physical effects in the optical spectra. For adsorbed molecules, the dipolar approximation might be sufficient, and the optical spectra might provide information about the molecular electronic structure and charge-transfer effects. On the other hand, supported particles are usually described by a macroscopic dielectric function, thus particle shape, multipolar coupling, and local-field effects become the main features to look for in the optical response. The calculation of all these effects has required the construction of more sophisticated theories beyond the simple image-dipole model. In the case of supported particles, the development of a more realistic model has required both, the treatment of the MC between the sphere and the substrate as well as the extension to nonspherical particles.^{6-9,11,14,15} In the electromagnetic effect in surface enhanced Raman spectroscopy, although the emphasis has been on the calculation of the induced field at adsorption sites, either on nonflat metallic surfaces or free-standing particles of very different shapes, one can also find some elaborate calculations of the field around a sphere above a flat substrate.^{16,17}

One of the objectives in the optical properties of supported particles has been the calculation of the exact *effective* polarizability of the supported particle, which takes into account the contributions to the induced dipole coming not only from the image dipole but also from the MC with the substrate. The main effect is the appearance of additional resonances, which correspond to the resonant coupling with modes with a multipolar character. However, despite the numerous experimental investigations of the optical response of supported particles, such additional resonances have not been observed experimentally so far. Since most of the experiments^{1,2,4,14} have been done with noble-metal particles, it is possible to conjecture that the isolation of the expected

resonances has been hindered by the efficient damping mechanisms present in these materials, as well as the strong influence of interband transitions which, for example in the case of silver, are responsible for the close proximity of the dipole and the expected higher-multipole resonant frequencies. Also, the use of substrates like quartz^{1,3,4}, which yields a small MC effect as we will show below, might have not been the optimum choice. An alternative solution would be the use of alkali-metal particles due to its free-electron character and moderate damping.

In this paper we present an experimental demonstration of the existence of substrate-induced multipolar resonances in small metallic particles by use of a differential reflectance (DR) spectroscopy on small potassium particles obtained by deposition on an oxidized silicon substrate. The oxide layer prevented direct chemical contact between potassium and silicon, yielding the formation of particles. Here we will present results only for small K depositions where the particles can be regarded as isolated. The reasonable agreement between the DR spectra and calculated spectra, using a model which incorporates MC, lead us to conclude that the additional peak in the DR spectra corresponds to multipolar resonances.

The silicon substrates were prepared by chemical etching and oxidation, following the procedure of Ref. 18, and this resulted in the formation of a silicon dioxide layer, whose thickness was 2.2 ± 0.2 nm, as measured by ellipsometry. K was evaporated from a SAES getter source, with a base pressure in the chamber of 1×10^{-10} mbar. The flux Φ_K of K atoms arriving at the surface was estimated to be $\sim 10^{-2}$ atom/nm²/sec. This estimate was reached by determining the time needed to obtain a saturation layer of K on a Si(111) 7×7 surface under the same experimental conditions.^{19,20} The optical measurements were performed during the K deposition by use of an *in situ* DR spectrometer,²¹ which delivers the relative change of reflectivity of the substrate upon deposition of K; that is,

$$\frac{\Delta R_p}{R_p} = \frac{R_p[\text{K/Si}] - R_p[\text{Si}]}{R_p[\text{Si}]}, \quad (1)$$

where $R_p[\text{K/Si}]$ and $R_p[\text{Si}]$ are the reflectivities of the oxidized silicon substrate with and without potassium, respectively. The experiments were performed in *p* polarization, at an angle of incidence $\theta = 60^\circ$. Several experiments have been performed for different substrate temperatures between -120 and 45°C , and all of them gave qualitatively the same results.

In the very first stages of K deposition, a certain amount of K atoms migrate through the oxide down to the SiO₂/Si interface, where they remain as K⁺ ions, as shown by Auger spectroscopy and by DR measurements.²² After this initial stage, the migration of K atoms stops and particle formation starts on the surface of the oxide. In Fig. 1 we show three experimental spectra of $\Delta R_p/R_p$ as a function of photon energy $\hbar\omega$, after 60, 90, and 120 sec from the initiation of K particle formation on a substrate maintained at -80°C . They display a well defined peak around 1.8–1.9 eV, and a very distinctive feature above ~ 2.3 eV. An additional spectrum obtained at 37°C is also drawn in Fig. 1, showing the same general shape. To make the 2.3-eV feature more evi-

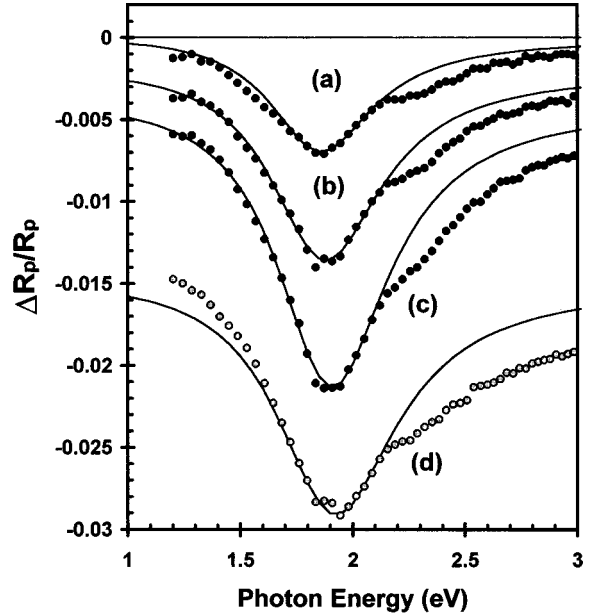


FIG. 1. Experimental DR spectra for increasing amounts of K deposited on oxidized Si surfaces. (a)–(c) substrate temperature -80°C ; times of deposition 60, 90, and 120 sec. (d) substrate temperature 37°C ; time of deposition 70 sec. Spectra (b), (c), and (d) have been shifted by -0.002 , -0.004 , and -0.015 , respectively. The continuous lines are guides for eye.

dent to the eye, we have drawn continuous curves fitted to the data by assuming a single Lorentzian resonance in the dielectric response of the film.

At optical frequencies bulk potassium behaves as a free-electron metal with a dielectric function of the Drude type, with a plasma frequency ω_p given by $\hbar\omega_p \approx 3.8$ eV.²³ Thus the frequency of the dipolar resonance of a free-standing K sphere is $\hbar\omega_p/\sqrt{3} \approx 2.19$ eV. For very small free-standing K clusters, the dipolar resonance has been observed between 1.93 and 2.1 eV.²⁴ Since the main features of our experimental spectra lie around 1.9–2.3 eV, one can assume with confidence that they should come from plasma resonances in deposited K particles. Furthermore, estimates of the amount of deposited potassium lead us to conclude that the number of particles per unit area is low enough so one can consider that the particles do not interact with each other. For example, assuming that a spherical particle of radius R has $2 \times 4\pi/3 (R/a_L)^3$ atoms, one can estimate that for spectrum (a) shown in Fig. 1, the two-dimensional filling fraction $f_2 = N\pi R^2/A$ is around $\sim 3 \times 10^{-3}$, when one takes the flux of K atoms as $\Phi_K \sim 10^{-2}$ atoms/(nm² sec), and assumes that the particles have a radius $R \sim 10$ nm. Here $a_L = 0.525$ nm is the lattice constant of solid K, N is the total number of spheres deposited on an area A , and the value $R \sim 10$ nm was chosen because it is about the actual size of the deposited particles, as will be concluded below. Moreover, the interaction among particles sets up coupled modes in the system whose frequencies are blueshifted from the frequencies of the isolated particles.¹⁰ Since in the spectra shown in Fig. 1 the position of the peaks does not show any appreciable shift, this fact is in agreement with the idea that we are dealing with noninteracting particles. Therefore, the profile of the

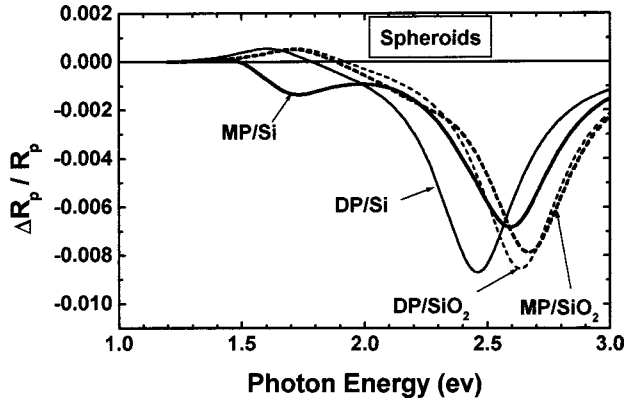


FIG. 2. Calculated DR spectra for K oblate spheroids with an aspect ratio $r_o=2$. (1) On top of Si: dipolar calculation (thin continuous line) and multipolar calculation (thick continuous line). (2) On top of SiO₂: dipolar calculation (thin dashed line) and multipolar calculation (thick dashed line).

DR spectrum should depend only on the shape of the particles and their interaction with the substrate.

Although a direct observation of the size and shape of the particles was not possible due, essentially, to their instability, a couple of facts suggest that the particles might be close to be spherical: (i) The particles are not stable at room temperature and they re-evaporate, as determined by the decrease of the DR signal after stopping the deposition;²⁵ thus one might expect that they are close to their free equilibrium spherical shape. Since the shape of DR spectra at low temperatures does not change, one might expect that the shape of the particles does not change either. (ii) Taking oblate spheroids (OS's) as the simplest possible model for a supported flat island, calculations of the DR spectra, shown below, yield a main negative peak at frequencies which are too high relative to the frequency of the main peak in the experimental spectra.

The calculations of $\Delta R_p/R_p$ were done for OS's with their symmetry axes perpendicular to the interface. In the low density limit ($f_2 \ll 1$), and in cgs units, $\Delta R_p/R_p$ is given by⁵

$$\frac{\Delta R_p}{R_p} = 16 \frac{\omega a}{c} f_2 \cos \theta \operatorname{Im} \left[\frac{(\epsilon_B - \sin^2 \theta) \tilde{\alpha}_{\parallel} - \epsilon_B^2 \sin^2 \theta \tilde{\alpha}_{\perp}}{(1 - \epsilon_B)(\sin^2 \theta - \epsilon_B \cos^2 \theta)} \right], \quad (2)$$

where ϵ_B is the dielectric function of the substrate; $\tilde{\alpha}_j \equiv \alpha_j/ab^2$ ($j=\perp, \parallel$); α_{\perp} and α_{\parallel} are the effective polarizabilities of the supported K particles for fields perpendicular (\perp) and parallel (\parallel) to the interface; $2a$ and $2b$ are the minor and major axes of the OS's, respectively; and c is the speed of light. The two-dimensional factor f_2 is now equal to $N\pi b^2/A$. The dielectric function for Si was taken from Ref. 26, for SiO₂ we took $\epsilon_B=2.25$, and for potassium we adopted a Drude model $\epsilon(\omega)=1-\omega_p^2/(\omega^2+i\omega/\tau)$ with $\hbar\omega_p=3.8$ eV (Ref. 23) and $\Gamma \equiv \hbar/\tau=0.4$ eV. Our choice of $\Gamma=0.4$ eV, is supported by recent photoabsorption experiments on beams of ionized K clusters.²⁴ Using the formalism developed in Ref. 9, the calculations of $\tilde{\alpha}_{\parallel}$ and $\tilde{\alpha}_{\perp}$ of a supported OS were done to a given spheroidal-multipolar order L , until convergence was attained. In Fig. 2 we show $\Delta R_p/R_p$ as a function of energy for an OS of K with aspect

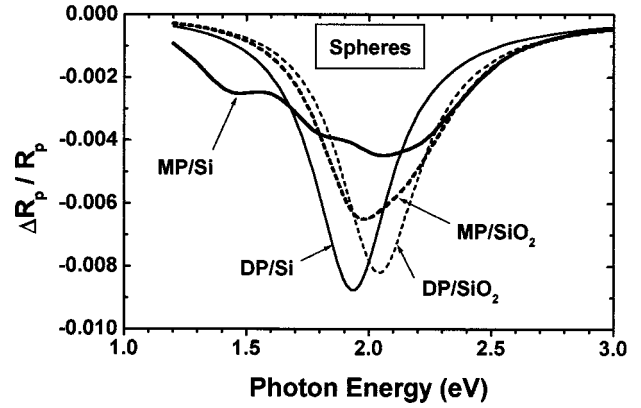


FIG. 3. Calculated DR spectra for K spheres. (1) On top of Si: dipolar calculation (thin continuous line) and multipolar calculation (thick continuous line). (2) On top of SiO₂: dipolar calculation (thin dashed line) and multipolar calculation (thick dashed line).

ratio $r_o \equiv a/b=2.0$. Throughout this paper, the effective polarizabilities were calculated as if the spheroid were on top of either a Si or a SiO₂ substrate but the DR spectra were calculated taking the clean Si substrate as a reference. In Eq. (2) we used $af_2=0.0023$ nm, in order to attain numerical agreement with the data. af_2 gives a measure of the amount of K atoms, and is independent of the particle shape. This value of af_2 is about ten times smaller than the one expected from the estimations of the amount of potassium deposited on the substrate. One reason for this is that the calculated spectrum is narrower than the experimental spectrum (a), likely due to some dispersion in the shape of the actual particles. Moreover, it indicates that the sticking coefficient of K should be smaller than 1. We also plot the DR spectra in the dipolar approximation ($L=1$). One can see that, for the OS on top of the SiO₂ substrate, the MC has a minor effect. Conversely, for Si, the resonance observed at 2.45 eV for the dipolar approximation is shifted to 2.6 eV, and a small multipolar resonance appears at ≈ 1.7 eV. The important point is that for both substrates, when the MC is considered, the main resonance is located at ≈ 2.6 eV, which is much higher than the experimental observation. For an OS with smaller aspect ratio, the main resonance lies at smaller energies (e.g., 2.4 eV for $r_o=1.5$). This provides us with strong evidence to rule out the possibility that the K particles under investigation could be flat, and to consider rather that their shape is close to be spherical. Therefore, in the following we will simplify our analysis by regarding the shape of the supported K particles as spherical.

In order to see the effect of the interaction with the substrate, in Fig. 3 we have drawn the spectra of $\Delta R_p/R_p$ for a K sphere on top of Si or SiO₂ in the dipole approximation. A single symmetric deep minimum peaks at 1.9 eV (2.05 eV) for the Si (SiO₂) substrate, but no distinctive shoulder is observed on the high-energy side of the minimum. In Fig. 3 we also show the DR spectra calculated by taking account of MC to all orders. The effective polarizability was calculated using the formalism developed in Ref. 8. Actually, in order to avoid problems related to multipolar convergence, in the case of the Si substrate, the calculation was performed for a sphere located at a distance $R+\delta$ above the substrate with

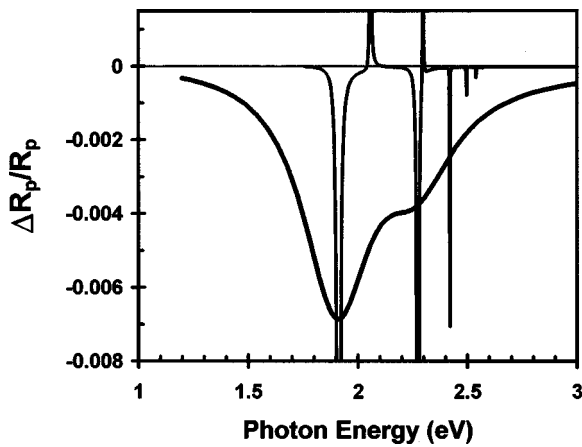


FIG. 4. Calculated DR spectra for K spheres above Si ($D/R = 0.12$). Thick line: damping parameter $\Gamma = 0.4$ eV; thin line: $\Gamma = 0.0004$ eV.

$\delta/R = 0.01$. In this case convergence was attained for $L = 36$. In the case of the SiO_2 substrate there were no convergence problems for $\delta = 0$, and convergence was attained for $L = 12$. For SiO_2 , this yields a small broadening of the minimum with an asymmetric shape, not large enough to reproduce the experimental shoulder. Conversely, for the Si substrate, the spectrum differs markedly from the one corresponding to the dipolar approximation ($L = 1$), with a broadening and the appearance of rich resonant structures, showing in this case the importance of the MC. However, this spectrum does not compare with the experiments on Fig. 1. At this point we recall that the Si substrate is coated by a thin layer of SiO_2 , which decreases the Si interaction with the K sphere. For simplicity, we will assume that the main effect of this layer is to keep the particle a certain effective distance D above the Si substrate, where D is close to the actual thickness d of the oxide layer. Using the same formalism,⁸ we show now in Fig. 4 the DR spectrum for spheres located a distance $D/R = 0.12$ above the silicon substrate. This value corresponds to spheres of radius around 18 nm. The shape of the DR spectrum now resembles the experimental one quite closely. With the chosen parameter ($a f_2 = 0.0023$ nm) the profile of the main minimum and the distinctive shoulder agree fairly well with the data of the 60-sec spectrum, differing only in the wider low- and high-energy tails of the experimental spectrum. In order to show that the distinctive shoulder in the DR spectrum is actually a remnant of well-defined multipolar resonances which have been broadened by dissipative effects, in Fig. 4 we also show the DR spectrum calculated with the same parameters but with $\Gamma = 0.0004$ eV. There is a series of very sharp positive and negative peaks, coming from the resonances of $\tilde{\alpha}_{\parallel}$ and of

$\tilde{\alpha}_{\perp}$, respectively. For each negative peak there is a blue-shifted positive one. This is seen in only two peaks in the figure due to resolution. The negative peaks have a greater strength than the corresponding positive ones, which simply means that the external field couples more strongly with the perpendicular modes. This is the reason why when Γ increases the overall spectrum is negative. Also for large values of Γ the positive resonances appear either as negative minima, enhancing the distinctiveness of the negative maxima, or as inflection points in the profile. Finally, we have to mention that the remaining discrepancy between the experimental spectra and the calculated one in Fig. 4, namely, the high-energy tail, is likely due to the scattering of light by the particles, which has not been taken into account here. We have checked that a simple Rayleigh scattering, varying as ω^4 , permits one to reproduce this additional tail correctly. On the other hand, the larger width of the experimental spectra (~ 0.6 eV) likely results, as mentioned above, from a distribution of shapes of the particles around the spherical one.

In conclusion, we have shown that multipolar-coupling effects due to the interaction with the substrate occur in the optical response of supported metallic particles. The choice of a quasi-free-electron metal as potassium and a high-dielectric function substrate like silicon gave us the possibility to clearly observe an interesting feature in the DR spectra, close to the main dipolar resonance. The use of a theoretical model, taking into account the multipolar interaction between the K particles and the substrate, allowed us to assign this feature to the excitation of multipolar resonances. This result is important because optical techniques are now widely used for studying and monitoring metallic growth. For substrates with small dielectric response, like silica, the effect is small. Conversely, when the dielectric response of the substrate is large, as in metals and semiconductors, these MC effects have to be taken into account. Furthermore, they can provide information about the morphology of the deposited metal film from the optical data. This is still more crucial when the particles are not necessarily spherical, which is usually the case for metal film grown on a crystalline surface.

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¹T. Yamaguchi, S. Yoshida, and A. Kinbara, *Thin Solid Films* **21**, 173 (1974).

²H. G. Craighead and G. A. Niklasson, *Appl. Phys. Lett.* **44**, 1134 (1984).

³P. Tognini, M. Geddo, A. Stella, P. Cheyssac, and R. Kofman, *J. Appl. Phys.* **79**, 1032 (1996).

⁴See, for example, U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters* (Springer-Verlag, Berlin, 1995), and references therein.

⁵A. Bagchi, R. G. Barrera, and B. B. Dasgupta, *Phys. Rev. Lett.* **44**, 1475 (1980); A. Bagchi, R. G. Barrera, and R. Fuchs, *Phys. Rev. B* **25**, 7086 (1982).

- ⁶R. Ruppin, Surf. Sci. **127**, 108 (1983); Phys. Rev. B **45**, 11 209 (1992).
- ⁷B. N. J. Persson and A. Liebsch, Phys. Rev. B **28**, 4247 (1983).
- ⁸M. M. Wind, J. Vlieger, and D. Bedeaux, Physica A **141**, 33 (1987); M. M. Wind, P. A. Bobbert, J. Vlieger, and D. Bedeaux, Physica A **143**, 164 (1987).
- ⁹P. A. Bobbert and J. Vlieger, Physica A **147**, 115 (1987).
- ¹⁰R. G. Barrera, M. del Castillo, G. Monsivais, P. Villasenor, and W. L. Mochan, Phys. Rev. B **43**, 13 819 (1991).
- ¹¹See, for example, G. Bosi, J. Opt. Soc. Am. B **13**, 1691 (1996), and references therein.
- ¹²See, for example, W. L. Mochán and R. G. Barrera, Phys. Rev. Lett. **56**, 2221 (1986).
- ¹³G. Bader, P. V. Ashrit, F. E. Girouard, and V. V. Truong, J. Appl. Phys. **68**, 1820 (1990).
- ¹⁴D. Martin, J. Jupille, and Y. Borensztein, Surf. Sci. **402-404**, 433 (1998).
- ¹⁵B. R. Johnson, J. Opt. Soc. Am. A **13**, 326 (1996).
- ¹⁶P. K. Aravind, R. W. Rendell, and H. Metiu, Chem. Phys. Lett. **85**, 396 (1982).
- ¹⁷T. Takemori, M. Inoue, and K. Ohtaka, J. Phys. Soc. Jpn. **56**, 1587 (1987).
- ¹⁸A. Ishizaka and Y. Shiraki, J. Electrochem. Soc. **133**, 666 (1986).
- ¹⁹C. Beitia, Ph.D. thesis, University of Paris VI, 1998.
- ²⁰H. H. Weitering, J. Chen, N. J. DiNardo, and E. W. Plummer, Phys. Rev. B **48**, 8119 (1993).
- ²¹Y. Borensztein, T. Lopez-Rios, and G. Vuye, Appl. Surf. Sci. **41/42**, 439 (1989).
- ²²C. Beitia and Y. Borensztein (unpublished).
- ²³D. W. Lynch and W. R. Hunter, in *Handbook of Optical Constants of Solids II*, edited by E. D. Palik (Academic Press, San Diego, 1991).
- ²⁴C. Bréchnignac, P. Cahuzac, N. Kebaili, J. Leygnier, and A. Sarfati, Phys. Rev. Lett. **68**, 3916 (1992).
- ²⁵C. Beitia and Y. Borensztein, Surf. Sci. **402-404**, 445 (1998).
- ²⁶D. E. Aspnes and A. A. Studna, Phys. Rev. B **27**, 985 (1983).