Spin-glass properties of metallic nanoparticles conducted by quantum size effects

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Diamagnetic silver reveals spin-glass properties as the material is dispersed into nanoparticles embedded in dielectric media. Significant shifts of the transition temperature T_{SG} toward high temperatures with the filling factor are observed during the zero-field-cooling process for the magnetic susceptibility $\chi(T)$ measurement. The diffused quantum-sphere model is exploited to calculate the susceptibility of nanoparticles containing even or odd numbers of electrons in terms of particle sizes, which manifests a paramagnetic Curie-like characteristic as the temperature rises above T_{SG}. The partition function evaluated by the spin-glass magnetic-dipole interaction conducted by quantum size effects can successfully address the experimental data with good quantitative agreement. [S0163-1829(99)08601-4]

Recently, many scientists[1–12] have devoted their efforts to the study of electronic properties of metallic nanoparticles, expecting to obtain a right perspective to the essential features of low-dimensional quantum confined electronic systems. The exotic characteristics of metallic nanoparticles are manifested by their optical,[1–5] electrical,[6–8] and magnetic[9–12] properties. Concerning the magnetic susceptibility, the derivation of partition function for a given electronic system from the thermodynamic approach is inevitable. The fundamental result in Kubo's model[13] indicates that the susceptibility depends on the selected ensemble under considerations of metallic particles containing either ''odd'' or ''even'' numbers of electrons.[14–16]

In spite of the many years of study of the physical properties of one single small metallic particle, the physics emanated from the interaction between particles remains neglected even in the recent literature.[6–8,12] The crucial factor that determines the interaction of particles in the filling factor f (or the concentration c), which is defined as the volume ratio of the total metallic particles to the volume of the samples.[8] In the detection of optical absorption, a filling factor below 0.001 is used to suppress the multiscattering and interaction between adjacent particles. The measurement of Bloch-Grüneissen-type electrical conductivity can be expected[6,7] if the filling factor is increased. A considerable extent of aggregation resulting from the large value of the filling factor gives rise to anomalous breaks in the resistance-temperature curves.[6,7] The Kondo spin-flip scattering of conduction electrons by metallic nanoparticle behaving similar to local spins[8] is tacitly assumed to explain the break around the critical transition temperature T_k. In the magnetic susceptibility $\chi(T)$ measurement, an exotic cusp is also observed[8,12] at the phase transition temperature T_{SG}. The commensurable transition temperatures in the magnetic property encourages us to propose a long-range spin-glass-like interaction between metallic nanoparticles.

The spin-glass system is a collection of random orientations of local spins which are frozen at low temperatures. The widely studied spin-glass system[17–19] is composed of dilute solutions of magnetic transition metal impurities distributed in nobel metal hosts. The interactions between these randomly distributed impurities usually exhibits a Ruderman-Kittel-Kasuya-Yosida (RKKY) oscillation.[17–19] The $\chi(T)$ curves exhibit marked cusps at the temperature which defines the frozen temperature $T_f(T_{SG})$, suggesting a second-order phase transition between a disordered paramagnetic state and a frozen spin-glass state characterized by the distinguished curves between the ''zero-field-cooling'' and ''field-cooling'' processes as shown in Fig. 1. The $\chi(T)$ curve in Fig. 1 is obtained from the experimental data[12] which has been substrated by the Curie-type contribution of the background signal which is due to the impurity in the SiO_2 substrate. According the the model of broken ergodicity and replica symmetry breaking, the local susceptibility of the spin glass is given by[19]

$$\chi(T)=\beta\left[1-\int_0^1 q(x)dx\right], \tag{1}$$

where $\beta=kT$ and q is the mean-square value of the local magnetization over the distribution, which satisfies a self-consistent equation at equilibrium such as

$$|\theta|-xq(x)-\int_x^1 q(y)dy+q^2(x)=0, \tag{2}$$

where $\theta=(T-T_f)/T_f$. It can be shown that $\int_0^1 qxdx\sim|\theta|+|\theta|^2-|\theta|^3+O(|\theta|^4)$ for T near T_f.

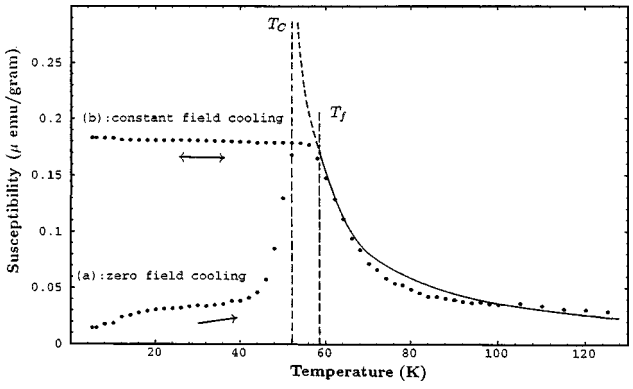

FIG. 1. The plot of $\chi(T)$ as functions of temperatures for silver nanoparticles with $R=46.8$ Å, $f=0.00598$, and $\sigma=1.30$, where σ is the width of the log-normal distribution. The points are the experimental data, and the solid curve is fitted with $T_f=54.1$ K, $T_C=45.0$ K, and $\beta=0.38$. The dashed curve below T_f indicates Curie-Weiss behavior extended from the range $T\geqslant T_f$.

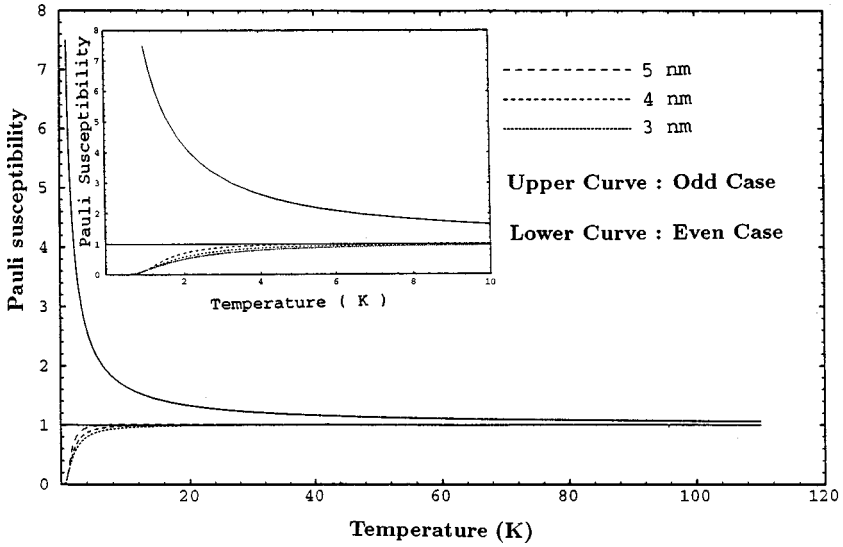

FIG. 2. The magnetic susceptibilities for metallic particles with ''odd'' and ''even'' numbers of electrons. The curves are calculated from the QSM which are normalized to the Pauli spin susceptibility. The inset is the expanded view below 10 K.

For the magnetic susceptibility detection of small metallic particles as shown in Fig. 1, the Curie-type behavior about T_f is attributed to the paramagnetic alignment of the randomly oriented local spins for particles with an odd number of electrons with values which are compatible with the prediction of Kubo's theory.[13] At temperatures below T_f, the dipolar interaction between local spins overwhelms the paramagnetic term, resulting in a similar RKKY-type[17–19] oscillation. Therefore, the critical temperature T_f ensuing the commensurability between paramagnetic and spin-glass states is observed in this work.[8,12]

This work appraised the magnetic susceptibility of small metallic particles within the temperature range of two distinct magnetic phases. The variation of the critical transition temperature T_f is examined and found to be related to the filling factor *f*. This evidence is verified by the theory of the quantum-sphere model (QSM)[4] in conjunction with the Sherrington-Kirkpatrick (S-K) model.[20]

The magnetic susceptibility χ can be evaluated from the partition function *Z* and the allowed transitions between electronic levels ε_m. The grand canonical partition function can be obtained by implementing the formula given by Kubo[13]

$$Z(H,T)=\frac{1}{2\pi i}\oint\frac{dz}{z}z^r\prod_{m=0,s=\pm1}^{p-1}\times\left[1+\left(\frac{1}{z}\right)e^{s\zeta}e^{-\beta\eta_m'}\right]\prod_{k=p}^{\infty}[1+ze^{s\zeta}e^{-\beta\eta_k}],\qquad(3)$$

where the energy levels ε_m's are ordered with $\varepsilon_1\leqslant\varepsilon_2\leqslant\varepsilon_3\leqslant\cdots$, ε_p is the uppermost occupied level at $T=0$. The ground state energy is $E_0=2\Sigma_{m=1}^{p}\varepsilon_m-r\varepsilon_p$, where $r=0$ for an even number of electrons and $r=1$ for an odd number of electrons, $\eta_m'=\varepsilon_p-\varepsilon_{p-1}$, $\eta_k=\varepsilon_{p+k}-\varepsilon_p$, $\xi=(\frac{1}{2})\beta g\mu_B H$, H is the applied magnetic field, β is equal to $(k_BT)^{-1}$, g is the Landé g factor, μ_B is the Bohr magneton, and z is a dummy variable in the integral. For simplification, most works[13–16] implemented the assumption by taking different ensembles of states with equal level spacing. Consequently, one has $\varepsilon_n=n\delta$, for $n=0,1,2,\ldots$, and δ is the spacing of each energy level η_n. The partition function under this simplified configuration can be rewritten in the form[13–16]

$$Z_{\text{even}}(H,T)=\left[1+2\sum_{n=0}^{\infty}e^{-\beta\delta(n+1)^2}\cosh[2(n+1)\zeta]\right]Z_B^2,\qquad(4)$$

$$Z_{\text{odd}}(H,T)=\left[2\sum_{n=0}^{\infty}e^{-\beta\delta n(n+1)}\cosh[(2n+1)\xi]\right]Z_B^2,\qquad(5)$$

with

$$Z_B=\prod_{n=1}^{\infty}[1-e^{-\beta\delta n}]^{-1},\qquad(6)$$

where Z_B is the canonical partition function for spinless fermions and the subscripts even and odd denote the even and odd number of electrons which are confined inside small metallic particles.

To yield a correct solution of the eigenenergies ε_m, the diffused quantum-sphere-model[4,21] in which the total potential $V_T(r)$ (Ref. 22) is evaluated by a self-consistent process consisting of the electrostatic and the exchange-correlation parts is implemented to solve the wave equations.[22] Accordingly, the eigenenergies ε_m's for a diffused surface were numerically simulated for both the filled and empty states.[21]

The magnetic susceptibility χ is given by

$$\chi=\beta^{-1}\frac{\partial^2}{\partial H^2}\ln Z,\qquad(7)$$

where $\beta=(k_BT)^{-1}$and Z is the grand canonical partition function. With the values of the partition function *Z* and the spectrum ε_m, the magnetic susceptibility can be numerically simulated as sketched in Fig. 2. The magnetic property of the system for an odd number of electrons leads to Curie-law behavior, while the even case yields an exponentially attenuated value. A paramagnetic background with Curie-Weiss behavior always coexists for the pure glass substrate arising from dangling bounds or defects in the SiO_2 glass prepared by the sol-gel method.[8,12]

Another aspect for the correlation between individual metallic particles may possibly arise from the existence of the dipolar interaction. Unlike the interaction due to the aggregation and thermal tunneling in the electrical property, the magnetic dipolar interaction ubiquitously persists for a longer range than those in the electrical conduction.[8] The

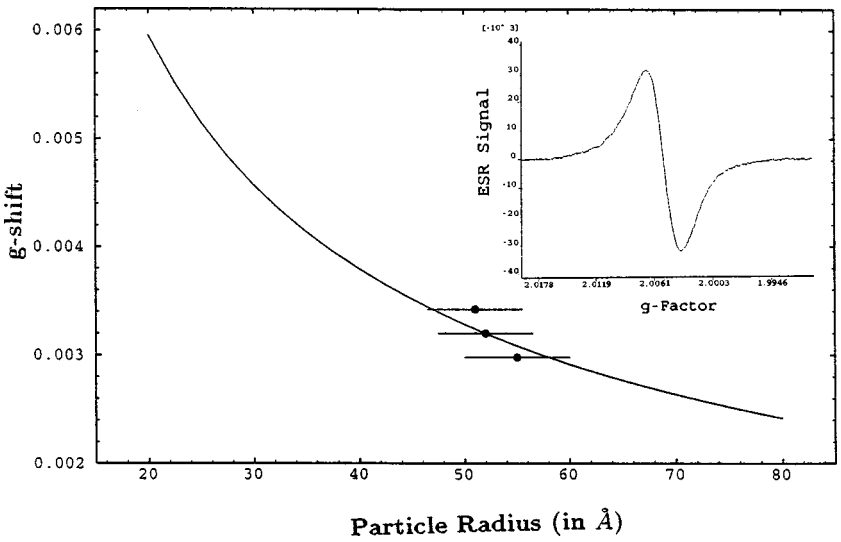

FIG. 3. The g shift (δg) for silver particles as a function of the radius in the diffuse QSM. The inset shows the EPR spectrum for silver particles embedded in glass with a mean size $\bar{R}=52.3$ Å. The $\delta g=$measured g, 2.0023. The three points are related to $\delta g=0.00320$ for $\bar{R}=52$ Å, $\delta g=0.00298$ for $\bar{R}=55$ Å, and $\delta g=0.00342$ for $\bar{R}=51$ Å, respectively.

relation[23] between the filling factor f and the distance between magnetic ions R_{ij} is $f\propto 1/R_{ij}^3$.It is known from the thermodynamics that[23]

$$f=A(D/J_{ij})^2\exp(-D/2|J_{ij}|), \tag{8}$$

where A is a constant, J_{ij} is the exchange integral between two local spins, and D is the typical conduction electron band widths range from 10^3 to $10^4\times k_B$. It is evident that the filling factor increases as the exchange integral is increased. We can trickily assume that $f\propto T_{ij}$. On the other hand, the SK model reconciled with the random energy approximation can express the critical temperature as[18–20] $T_f\propto J_{ij}$.

Because the spin-glass state has also been found in magnetic insulator and amorphous alloys, in which the dependence of the interactions on the separation of magnetic moments is entirely different from that for dilute magnetic impurities in nobel metal hosts. We can sophisticatedly presume that the metallic nanoparticles follow the more accurate relationship as $T_f\propto f$ which can be justified in this experimental work.

The spin system of the metallic particles can be elucidated more fully by the experiments of electron spin resonances. For bulk metals due to the strong spin-orbit interaction and extremely narrow skin depth, only the conduction electron spin resonance (CESR) signals can be observed in the finely dispersed particles ($\sim\mu$m in size). However, in the nanometer metallic particles, what we observed is not CESR even though it is similar to the line shape of free radicals. The g shift as given by the average of the orbital angular momentum induced by the spin-orbit interaction at the top of the Fermi distribution can be determined.[24]

The quantum sphere model disentangles the intricate problem and yields the unique solution[25]

$$\delta g(R)=\delta g(\infty)+4\sum_{m\neq n}\frac{|\langle\psi_{n\uparrow}|H_{\mathrm{SO}}|\psi_{m\downarrow}\rangle^2|}{(E_{mn})^2}, \tag{9}$$

where $\delta g(\infty)$ is the g shift of bulk material, $\psi_n(r,\theta,\phi)$ is the one-electron wave function obtained in Ref. 4, H_{SO} is the Hamiltonian due to the spin-orbit interaction, and E_{mn} is the energy difference between the m and n states. The positive g shift which is different than the negative g shift for bulk metals can be anticipated to be due to the diffuse of electron density outside the quantum sphere. The smaller the nanoparticles, the more diffuse the electrons outside of the surface. The lack of the electrons inside the sphere synaptically introduces a hole contribution to the g shift making a larger positive g shift as the particles size is reduced. The positive g shift evaluated at different particles sizes under the diffuse QSM is calculated as shown in Fig. 3, which is consequently in good agreement with the experimental values. Unfortunately, the particle sizes prepared by the sol-gel method are difficult to control, resulting in closely packed data.

The detailed preparation of small metallic particles by the sol-gel method was prescribed elsewhere.[8,12] The existence of Ag particles and the size distribution of various samples can be confirmed from the transmission electron microscopic (TEM) diffraction pattern and pictures as shown in Figs. 4(a), 4(b), and 4(c), respectively. The size distribution of

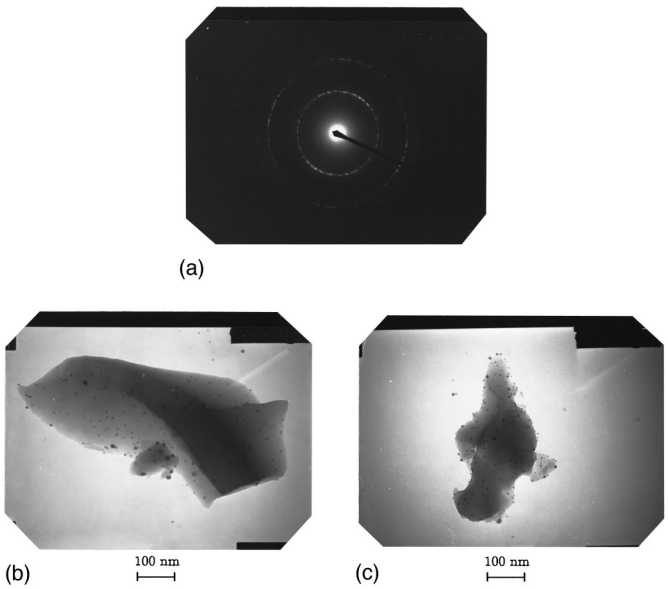

FIG. 4. (a) The TEM diffraction pattern shows the Bragg reflection from the Ag nanoparticles with two apparent rings for the ⟨111⟩ and ⟨200⟩ planes, showing that silver particles embedded in glass retains their virgin crystalline structure; (b) and (c) are the TEM images displaying size distribution of silver particles with concentrations of $AgNO_3$ at 0.1 and 0.05 g, respectively.

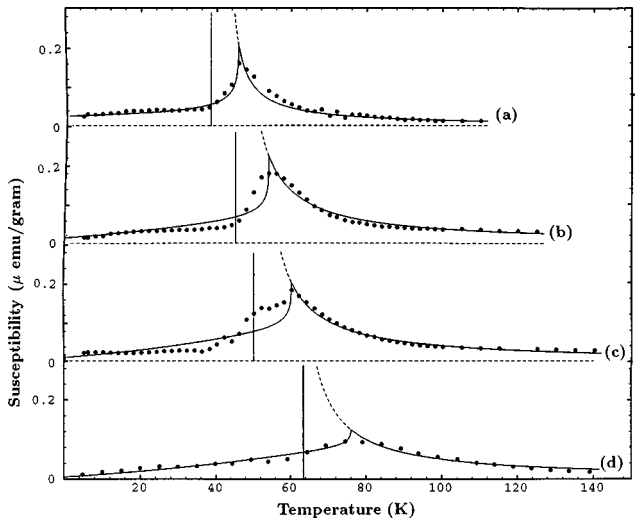

FIG. 5. The plot of magnetic susceptibilities versus temperatures for silver (a)–(c) and gold (d) nanoparticles with (a) $R=52.3$ Å, $\sigma=1.30$, $f=0.00567$, $T_C=38.5$ K, $T_f=46.2$ K, and $\beta=0.38$; (b) $R=46.8$ Å, $\sigma=1.30$, $f=0.00598$, $T_C=45.0$ K, $T_f=54.1$ K, and $\beta=0.38$; (c) $R=31.4$ Å, $\sigma=1.28$, $f=0.00620$, $T_C=50.1$ K, $T_f=60.3$ K, and $\beta=0.42$; and (d) $R=30.1$ Å, $\sigma=1.29$, $f=0.00671$, $T_C=63.4$ K, $T_f=76.0$ K, and $\beta=0.42$.

particles follows a log-normal function[8,12] which reveals the maximum probability radius R in these samples with sizes ranging from 3 to 6 nm.

The magnetic susceptibility as a function of temperature was measured from 4.2 to 140 K by a Quantum Design MPMS5 superconducting quantum interference device. The cusp illustrated in Fig. 1 suggests the possible presence of spin-glass-like behavior with a long-range dipolar interaction between the random distribution of metallic local spins. Figure 1 is simulated to yield $R=46.8$ Å, by implementing with the Curie constant $C=1.82\times10^{-5}$, the critical temperature $T_f=54.1$ K, the Curie temperature $T_C=45.0$ K, and the critical exponent $\beta=0.38$ for silver nanoparticles embedded in SiO_2 specified with a filling factor of $f=0.00598$. The Curie-type behavior, when the temperature is above T_f, occurs due to the paramagnetic property of small metallic particles.

A series of experimental curves with different values of normalized magnetic susceptibilities to the same ratio of Pauli susceptibility and the filling factor are compared in Fig. 5. Figure 5(d) is the result of gold nanoparticles prepared by $HAuCl_4\cdot H_2O$ in place of $AgNO_3$. The electrons contained in the gold nanoparticles can also be regarded as nearly free within an infinite potential barrier. Therefore the theoretical framework is similar to silver nanoparticles. The sample with the critical exponent $\beta=0.38$ has a large loss of dimension in comparison with that of $\beta=0.42$, and the reason can be deduced from the presence of sheetlike powder samples as shown in the TEM pictures. The critical temperature increases with the linear relation of the filling factor *f*, and is independent of the averaged particle size. Thus the most striking experimental feature as predicted in Fig. 5 is the salient increase of T_f with the filling factor *f* and is confirmed to exhibit a linear dependence of the critical temperature on the filling factor *f*, i.e., $T_f=c\times f$, where *c* is equal to 1.133×10^4 K.

In conclusion, we have prepared silver and gold nanoparticles embedded in silicate glasses using the sol-gel method. The susceptibility $\chi(T)$ derived from the diffused QSM (Refs. 4 and 21) can successfully explain the Curie-like behavior for temperatures about T_f. The nanoparticles containing an odd number of electrons lead to a Curie-type behavior on account of net unpaired spins. The decrease in the critical exponent β is characterized as the slight loss of dimensionality. The information extracted from the three-dimensional curves $\chi(T,f)$ can provide impressive insight into the quantum properties of metallic nanoparticles and evoke attention to properties of this material which have not been explored.

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[1] M. Fujii, T. Nagareda, S. Hayashi, and K. Yamamoto, Phys. Rev. B **44**, 6243 (1991).
[2] A. Berger, J. Non-Cryst. Solids **163**, 185 (1993).
[3] S. Zhou, I. Honma, H. Komiyama, and J. W. Haus, Phys. Rev. B **50**, 12 052 (1994).
[4] W. C. Huang and J. T. Lue, Phys. Rev. B **49**, 17 279 (1994).
[5] K. Y. Lo and J. T. Lue, Phys. Rev. B **51**, 2467 (1995).
[6] B. Roy and D. Chakravorty, J. Phys.: Condens. Matter **2**, 9323 (1990).
[7] A. Chatterjee and D. Chakravorty, J. Mater. Sci. **27**, 4115 (1992).
[8] J. T. Lue, W. C. Huang, and S. K. Ma, Phys. Rev. B **51**, 14 570 (1995).
[9] J. L. Millet and J. P. Borel, Surf. Sci. **106**, 403 (1981).
[10] S. Sako and K. Kimura, J. Phys. Soc. Jpn. **53**, 1495 (1984).
[11] F. G. Cherkasov, A. Ya. Vitol, and M. F. Galyautdinov, JETP Lett. **49**, 431 (1989).
[12] S. K. Ma and J. T. Lue, Solid State Commun. **97**, 979 (1996).
[13] R. Kubo, J. Phys. Soc. Jpn. **17**, 975 (1962).
[14] R. Denton and B. Mühlschlegel, Phys. Rev. B **7**, 3589 (1973).
[15] J. A. A. J. Perenboom, P. Wyder, and F. Meier, Phys. Rep. **78**, 173 (1981).
[16] W. P. Halperin, Rev. Mod. Phys. **58**, 533 (1986).
[17] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[18] T. Kaneyoshi, *Amorphous Magnetism* (CRC, New York, 1984).
[19] K. H. Fischer and J. A. Hertz, *Spin Glass* (Cambridge University Press, New York, 1991).
[20] D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. **35**, 1792 (1975).
[21] W. C. Huang and J. T. Lue, J. Phys. Chem. Solids **58**, 1529 (1997).
[22] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).
[23] D. C. Mattis, *The Theory of Magnetism* (Springer-Verlag, Berlin, 1981), p. 245.
[24] J. T. Lue, Nuovo Cimento B **26**, 243 (1975).
[25] J. Buttet and R. Car, Phys. Rev. B **26**, 2414 (1982).