Magnetic properties of spherical fcc clusters with radial surface anisotropy

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We have studied the magnetic properties of spherical fcc clusters at zero temperature using a numerical solution of the Landau—Lifshitz equations of motion with damping. Of particular interest is the effect caused by anisotropy which is uniaxial, radial, and present only on the surface. The hysteresis curves are obtained for different values of the anisotropy strength and for different cluster sizes. Insight into the spin-field configurations close to reversal is given. A specific dependence of the coercivity on the size of the clusters is found, which is explained qualitatively by the relative weight of the surface sites in the total number of sites in the cluster.

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I. INTRODUCTION

The magnetic properties of metallic clusters are not yet well understood[1-5]. The problem is complicated by the presence of surfaces and by the finite size of the system. Though the temperature dependence of the magnetization, the critical temperature, and the neutron-scattering cross section are modeled well by the isotropic Heisenberg model[6-8], experiments[3,5] suggests that the anisotropy energy per unit volume increases when shrinking the size of the cluster. The subject of the present paper is to study the influence of surface anisotropy on the hysteresis, the distribution of the spin field in a microscopic scale, and the transition to the state when the anisotropy can be neglected.[8,9]

The source of anisotropy could be the crystal field anisotropy or magnetic dipolar interaction, we do not consider the case of stress anisotropy. The dipole interaction is a long range interaction and thus it has negligible effect for clusters compared to the exchange term, where a cluster, in what follows, is assumed to consist of the order of tens to hundreds of atoms.[8] The crystal field anisotropy is expected to become even more important when decreasing the size of the cluster.[3,5] If one assumes for a spherical cluster the phenomenological expression for the effective anisotropy energy per unit volume[3]

$$K_{eff} = K_v + \frac{6}{D}K_s, \tag{1}$$

where K_v is the bulk anisotropy energy per unit volume, K_s is the surface density of the anisotropy energy, and D is the diameter of the cluster, then it is possible that the anisotropy energy per spin could become greater than the Heisenberg exchange coupling constant for small enough clusters. Effectively the increase of the anisotropy is associated with the increased importance of the surface of the cluster. This can be described quantitatively by the increased ratio of the number of surface spins to the total number of spins in the cluster when reducing its size. This ratio is presented in Table I for spherical fcc clusters up to the maximum size we have considered. We have used the fcc lattice as would be appropriate for Co clusters.[2,5] According to Chen et al.[5], the anisotropy energy per unit volume increases by more than an order of magnitude for $18\mathring{A}$ fcc Co clusters compared to the bulk value, namely from $2.7 \times 10^6 erg/cm^3$ for bulk to $3.0 \times 10^7 erg/cm^3$ for the $18\mathring{A}$ clusters. A similar enhancement of effective anisotropy is seen for α-Fe clusters.[3] We expect the effect of anisotropy to be stronger for fcc Co than for α-Fe clusters since the anisotropy energy per unit volume is approximately an order of magnitude larger for cobalt[5] than for iron.[3] In this paper we use estimates of the surface anisotropy from these experiments, and consider its effect on the magnetic hysteresis for a model spherical cluster. We also consider this model for a strength of anisotropy much stronger than that appropriate for Fe or Co clusters, to understand the influence of strong surface anisotropy.

The "spherical cluster" is built starting with a spin in the center of the sphere and then adding all other spins on the fcc lattice being closer to the central spin than a given distance which serves as the radius of the cluster. Hendriksen et al.[8] and Merikoski et al.[10] have considered recently spherical clusters constructed in the same way. The spins on the surface are in a different environment than the bulk spins — the presence of the surface breaks the translational symmetry and the number of nearest neighbors is reduced. The surface spins are defined as those spins of the cluster which do not have a number of nearest neighbor spins equal to the coordination number for the given lattice, in this case 12. Effectively the different environment at the surface changes the exchange coupling constant, the anisotropy strength, and the average magnetic moment per atom.[1-5,9]

The effect of varying the exchange coupling constant by allowing also more than just the nearest neighbor shells to interact, and the effect of varying the spin magnitude on the thermal magnetic properties have been studied by Lindgård and Hendriksen.[9] They have found only small deviations from the predictions[7,8] of the nearest neighbor isotropic Heisenberg model. The effects arising from the presence of anisotropy should be considered too, particularly for very small clusters, where a large fraction of the atoms are surface atoms. For fcc Co with a lattice constant[11] of 3.55Å, clusters having between 249 and 321 atoms will have diameters around 18Å(see Table I). Then the ratio of surface atoms to total number of atoms N_s/N_t is approximately 0.6. Thus more than half of the atoms are surface ones. Since with decreasing the size of the cluster the anisotropy energy per unit volume increases and also the ratio N_s/N_t increases one may assume that approximately all the anisotropy is associated with the surface sites and correspondingly the bulk sites have no anisotropy. We choose the anisotropy to be radial as suggested by the symmetry at the surface of the clusters[9] and also in accordance with the experimentally observed[12,13] normal surface anisotropy in the case of thin films.

II. THE MODEL

We consider a system of interacting classical spins on a fcc lattice in presence of an applied magnetic field. The Hamiltonian has the form,

$$H = -J \sum_{\mathbf{n},\mathbf{a}} \hat{\mathbf{S}}_{\mathbf{n}} \cdot \hat{\mathbf{S}}_{\mathbf{n}+\mathbf{a}} - K \sum_{\mathbf{n}_{\mathrm{s}}} (\hat{\mathbf{k}}_{\mathbf{n}_{\mathrm{s}}} \cdot \hat{\mathbf{S}}_{\mathbf{n}_{\mathrm{s}}})^2 - \sum_{\mathbf{n}} \mu \hat{\mathbf{S}}_{\mathbf{n}} \cdot \mathbf{H}. \tag{2}$$

The first term is the isotropic ferromagnetic ($J > 0$) Heisenberg exchange between the nearest neighbor spins. The second term is the coupling of the surface spins to a uniaxial anisotropy field ($\mathbf{n}_{\mathrm{s}}$ runs only over the surface sites). The coupling constants J and K are in energy units and the factor $\hbar^2 S^2$ is included in them which makes the $\hat{\mathbf{S}}_{\mathbf{n}}$'s dimensionless unit vectors. The anisotropy has constant coupling strength for all surface sites and the axes $\hat{\mathbf{k}}_{\mathbf{n}_{\mathrm{s}}}$ are assumed perpendicular to the surface of the cluster which in our construction is along the direction from the center spin site to the considered surface site. The last term is the coupling to the external magnetic field H, where μ is the magnetic moment per atom.

The classical equations of motion, that follow from the Hamiltonian Eq. (2), and the procedure for their numerical solution have been described in detail elsewhere.[14] Here we mention only that these are the well known Landau-Lifshitz coupled equations of motion with damping. The damping allows relaxation to a metastable state at zero temperature. We solve these equations numerically using a fourth-order Runge-Kutta scheme.

Although the simulation is for a single cluster, it should give also qualitative agreement with experiment in the case of clusters in a nonmagnetic matrix when first, the clusters are well isolated and the interaction among them can be neglected, and second, the deviation from the mean size of the clusters is small compared to the mean size itself. The data from the simulations can be related to the experimental data as follows. The value for the isotropic Heisenberg coupling constant J can be estimated from its expression in mean-field theory[11] $J = 3k_{\mathrm{B}}T_c/zS(S+1)$, where k_{B} is the Boltzmann constant, z is the coordination number, T_c is the Curie temperature, and S is the magnitude of the atomic spin in $\hbar$ units. The other parameters needed are taken directly from experimental measurements. We need the lattice constant, the diameter, the magnetic moment per atom or the saturation magnetization of the cluster, and the anisotropy energy per unit volume from which one can calculate K. For an order of magnitude estimate of K, we can multiply the area per surface atom (approximately a^2) times K_s, where K_s is taken from the experimental data available for the smallest clusters, using Eq. (1). For fcc Co, we get $J \approx 8$ meV, $K_s \approx 1$ erg/cm^2, $K \approx 0.8$ meV and therefore $K/J \approx 0.1$. This is considerably larger than the bulk value of $K/J \approx 0.0024$, but on an absolute scale it is weak surface anisotropy. Therefore we also consider $K/J > 0.1$, where the anisotropy has a much stronger effect.

III. RESULTS

First, we simulated different sizes of clusters, up to a cluster containing 459 spins, with the coupling constants ratio $K/J = 0.1$. For a cluster with total number of spins $N_t = 249$ and $N_s/N_t = 0.65$, K and J as estimated above for Co, and the magnetic moment per atom $\mu \approx 1.9\mu_B$ taken from the experiment[4] the hysteresis loop is shown in Fig. 1. The coercivity $H_c \approx 1000$ Oe is greater than the experimentally measured value[5] of approximately 639 Oe at 10 K. This result is expected because at $T \neq 0$ K the thermal fluctuations enhance the motion of the spins allowing better alignment to the external magnetic field. The magnetization follows the magnetic field closer at 10 K and the process of reversal is more continuous. At $T = 0$ the excess of thermal energy $k_{\mathrm{B}}T$ is not present, the magnitude of the magnetization does not change significantly up to the point of reversal where the magnetization jumps to its new

metastable state. The jump occurs when the energy associated with the coupling to the magnetic field exceeds the barrier due to the anisotropy interaction. The simulation shows that the magnetization does not saturate even 10 kOe. This is in agreement with the experiment at 10 K where fields of the same order of magnitude are not enough to reach saturation. This means that even at strong fields the surface spins equilibrate at directions between the direction of the magnetic field and their anisotropy axes and since the surface spins are more than half of the total number of spins in this cluster the effect is not small.

The anisotropy per unit volume increases with decreasing cluster size and we may expect that K/J could be even larger than 0.1. Also, for the fcc lattice, with the large bulk coordination number $z = 12$, fairly large values of K/J are required to produce significant hysteresis effects. Though larger values of K/J are more important when the size of the cluster is small, we have carried out the simulations for $0.1 \leq K/J \leq 10.0$ and for clusters with total number of spins ranging from 13 to 459. For clusters with more than 459 spins the behavior approaches the bulk limit.[4] We note that in this limit the effect of the surface decreases, primarily because the number of bulk sites becomes greater than the number of surface sites when $N_t > 459$.

Next we consider the effects of strong anisotropy ($K/J = 10.0$) on the hysteresis loop in the case of a cluster with total number of spins $N_t = 87$ and $N_s/N_t = 0.78$, see Table I. The reduced magnetizations per spin for the bulk spins, surface spins, and the mean magnetization are shown in Fig. 2. The hysteresis curve of the bulk spins represents the effect of the Heisenberg term in the Hamiltonian. If the bulk spins were not coupled to the spins at the surface, they would behave as a single spin in magnetic field, in which case they would reverse when the magnetic field **H** changes sign and no hysteresis would be observed. But due to the coupling to the surface spins the bulk magnetization also shows hysteresis with coercivity several times smaller than the coercivity of the surface spins. As a result the mean magnetization coercivity falls between these two values. Another effect due to the anisotropy is the difficulty to obtain saturation of the magnetization even at very strong fields. This is caused not only by the strong anisotropy but also by the relatively high weight of the number of surface spins N_s/N_t. Thus, at high fields the mean magnetization stays closer to the surface magnetization and shows lack of saturation while the bulk spins are already saturated.

On the microscopic scale the spins have lost their ferromagnetic order even at relatively strong external fields. The ferromagnetic order is broken as a consequence of the strong instability occurring on the surface by the uniaxial anisotropy. The distribution of the spins in a plane through the center of the cluster, perpendicular to the [001] direction and with the magnetic field along the [100] direction is shown in Fig. 3 for two values of the magnetic field as indicated with circles in Fig. 2. The first value of the field is before reversal of the mean magnetization and the second is after its reversal. The surface spins' reversal lags behind that of the bulk spins due to the strong anisotropy field to which they are coupled. In addition, they have less nearest neighbors, which reduces their coupling to the bulk. Therefore effectively the bulk spins are coupled stronger to the external magnetic field than the surface spins and they follow it closer. The irregular distribution of the surface spins close to reversal creates different potential barriers for different groups of spins on the surface to overcome towards their equilibrium distribution at high fields. Relaxing the different groups of surface spins leads to steps in the surface magnetization and thus in the mean magnetization too. The height of the step depends on the number of spins involved in the flip and on the magnitude of the flip. The creation of groups of spins is determined by the "discrete" structure of the surface. The spins having the smallest number of nearest neighbors will flip last.

An important quantity characterizing the hysteresis is the coercivity. The dependence of the coercivity, scaled by J/μ, as a function of the ratio K/J and the size of the clusters is shown in Fig. 4. This result shows explicitly the dependence of the coercivity on the relative weight of the surface sites N_s/N_t. The greater the ratio N_s/N_t the greater the coercivity at fixed K/J. The coercivity H_c decreases for $K/J \leq 1.0$, approaching values of the order of 1.0×10^{-3} (in units of J/μ) for $K/J = 0.1$, even for the cluster with N_s/N_t at maximum, namely for $N_t = 43$. In this case, at the coercive field the flipping of the bulk spins leads to an almost complete flip of the surface spins to their new equilibrium state. Thus for $K/J \leq 0.1$ and $T = 0$ K the cluster behaves approximately as a single spin.

IV. CONCLUSIONS

The zero temperature magnetic properties of metallic clusters with fcc structure have been studied using a classical Hamiltonian including Heisenberg exchange and radial uniaxial anisotropy on the surface. The Landau-Lifshitz equations of motion with damping have been solved numerically using a fourth-order Runge-Kutta scheme. The hysteresis shows strong dependence on the anisotropy when the anisotropy coupling constant K is greater than or equal to the exchange coupling constant J. We obtained a dependence of the coercivity on the relative weight of the surface spins in the total number of spins in the cluster N_s/N_t. Increasing N_s/N_t leads to increase of the coercivity with $K/J = constant$. The spins have lost the ferromagnetic order due to the instability on the surface. For small clusters and $K/J \geq 1.0$ the bulk spins reverse before the surface spins. Due to the "discrete" character of the surface,

group of spins on the surface reverse at different fields creating steps in the magnetization.
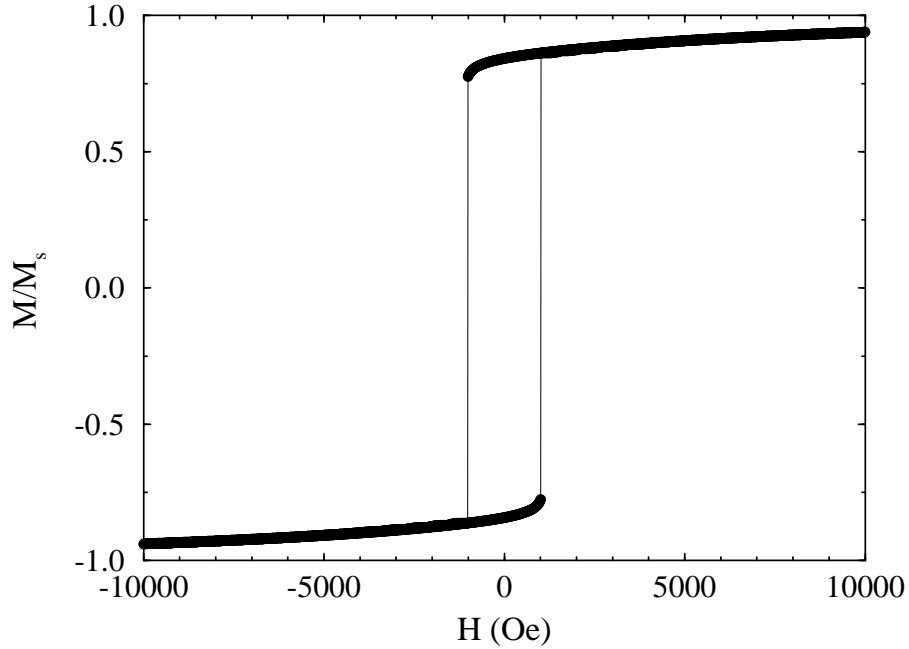
V. ACKNOWLEDGMENTS

FIG. 1. Hysteresis loop of the fcc cluster with 249 spins and coupling constants ratio $K/J = 0.1$
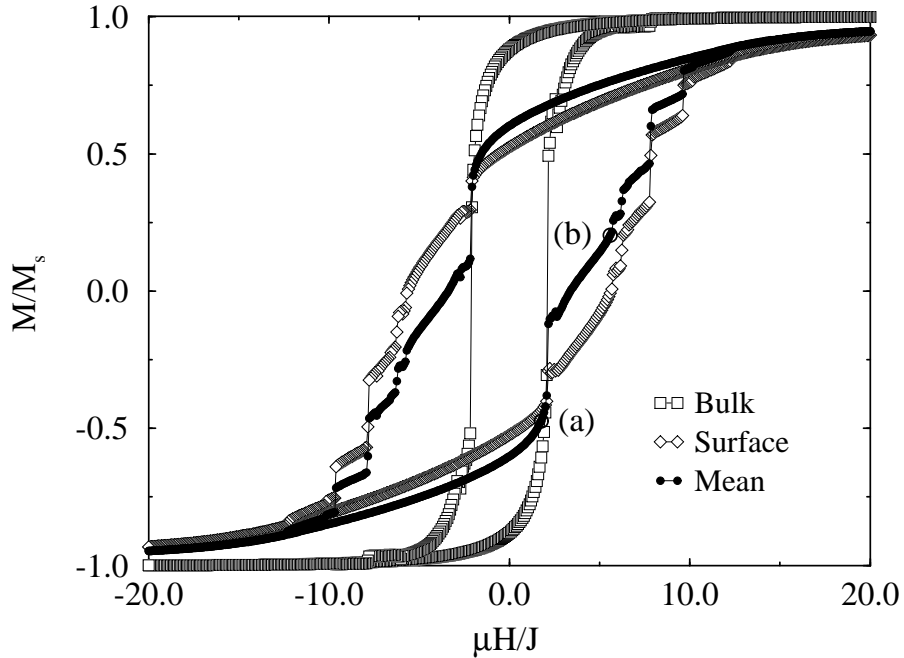

FIG. 2. Reduced bulk, surface, and mean magnetization per spin for a cluster with 87 spins and strong anisotropy, $K/J = 10.0$.

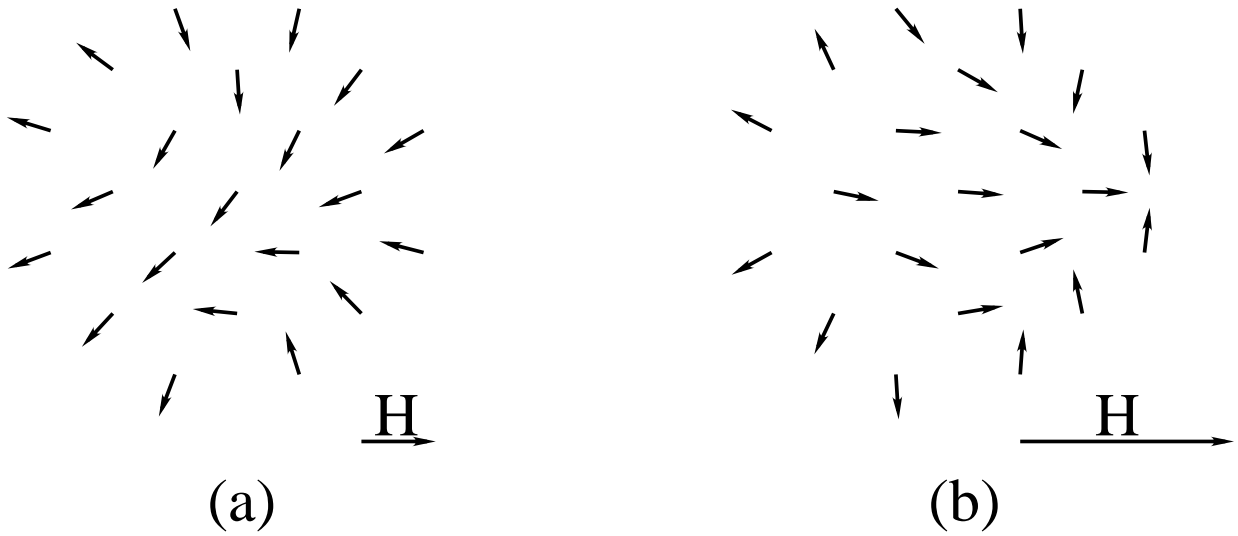FIG. 3. Spin field configurations for a group of the spins of the cluster having 87 spins with $K/J = 10$. The magnetic field is along the [100] direction and the spins are on the plane splitting the cluster through its center and perpendicular to the [001] direction. Only the projections of the spins on this plane are presented. (a) Corresponds to the first value of the field, $\mu H/J = 1.76$, indicated in Fig. 2. (b) For the second value of the field, $\mu H/J = 5.58$.
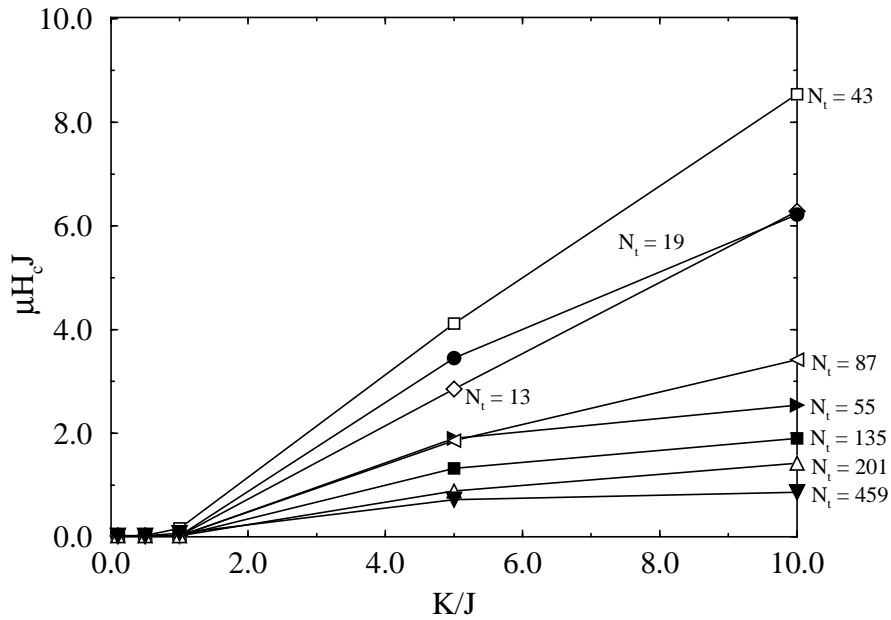

FIG. 4. Dependence of the reduced coercivity H_c, scaled by J/μ, on the coupling constants ratio K/J and on the number of spins in a spherical cluster with fcc structure.

TABLE I. Dependence of the ratio of number of surface sites to the total number of sites in fcc clusters. D is the diameter of the cluster, N_t denotes the total number of sites in it, and N_s is the number of surface sites.

D^{a}	N_t	N_s	N_s/N_t
1.415	13	12	0.923
2.000	19	18	0.947
2.450	43	42	0.977
2.829	55	42	0.764
3.163	79	60	0.759
3.465	87	68	0.782
3.742	135	92	0.681
4.001	141	98	0.695
4.243	177	122	0.689
4.473	201	122	0.607
4.691	225	138	0.613
4.900	249	162	0.651
5.100	321	180	0.561
5.478	369	204	0.553
5.658	381	204	0.535
5.832	429	228	0.531
6.001	459	234	0.510

[a]The diameter is in units a, where a is the lattice constant. Note that this is the minimum diameter with the specified total number of sites.

[1] W. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).

[2] J. P. Boucher, D. C. Douglass, and L. A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).

[3] F. Bødker, S. Mørup, and S. Linderoth, Phys. Rev. Lett. **72**, 282 (1994).

[4] I. M. L. Billas, A. Châtelain, and W. de Heer, Science, **265**, 1682 (1994).

[5] J. P. Chen, C. M. Sorensen, K. J. Klabunde, and G. C. Hadjipanayis, J. Appl. Phys. **76**, 6316 (1994).

[6] P. V. Hendriksen, S. Linderoth, and P.-A. Lindgård, J. Magn. Magn. Mater. **104-107**, 1577 (1992).

[7] P. V. Hendriksen, S. Linderoth, and P.-A. Lindgård, J. Phys. Condens. Matter **5**, 5675 (1993).

[8] P. V. Hendriksen, S. Linderoth, and P.-A. Lindgård, Phys. Rev. B, **48**, 7259 (1993).

[9] Per-Anker Lindgård and Peter V. Hendriksen, Phys. Rev. B **49**, 12291 (1994).

[10] J. Merikoski, J. Timonen, and M. Manninen, Phys. Rev. Lett. **66**, 938 (1991).

[11] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart & Winston, New York, 1976).

[12] K. B. Urquhart, B. Heinrich, J. F. Cochran, A. S. Arrot, and K. Myrtle, J. Appl. Phys. **64**, 5334 (1988).

[13] Z. S. Shan, D. J. Sellmyer, S. S. Jaswal, Y. J. Wang, and J. X. Shen, Phys. Rev. Lett. **63**, 449 (1989).

[14] D. A. Dimitrov and G. M. Wysin, Phys. Rev. B **50**, 3077 (1994).