# Temperature Dependent Magnetic Anisotropy in Metallic Magnets from an *Ab Initio* Electronic Structure Theory: $L1_0$-Ordered FePt

J. B. Staunton,[1] S. Ostanin,[2] S. S. A. Razee,[3] B. L. Gyorffy,[4] L. Szunyogh,[5] B. Ginatempo,[6] and Ezio Bruno[6]

[1]*Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*
[2]*Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom*
[3]*Department of Physics, Kuwait University, P.O. Box 5969, SAFAT 13060, Kuwait*
[4]*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*
[5]*Department of Theoretical Physics, Budapest University of Technology and Economics, Budapest, Hungary*
[6]*Dipartimento di Fisica, Universita di Messina, Salita Sperone 31, 98166 Messina, Italy*

(Received 29 July 2004; published 14 December 2004)

Using a first-principles, relativistic electronic structure theory of finite temperature metallic magnetism, we investigate the variation of magnetic anisotropy $K$ with magnetization $M$ in metallic ferromagnets. We apply the theory to the high uniaxial $K$ material, $L1_0$-ordered FePt, and find its magnetic easy axis perpendicular to the Fe/Pt layers for all $M$ and $K$ to be proportional to $M^2$ for a broad range of values of $M$. For small $M$, near the Curie temperature, the calculations pick out the easy axis for the onset of magnetic order. Our *ab initio* results for this important magnetic material agree well with recent experimental measurements, whereas the single-ion anisotropy model fails to give the correct qualitative behavior.

DOI: 10.1103/PhysRevLett.93.257204 PACS numbers: 75.30.Gw, 71.15.Rf, 75.10.Lp, 75.50.Bb

By accounting for relativistic effects such as spin-orbit coupling on electronic structure, recent ''first-principles'' theoretical work has succeeded in describing trends in the magnetocrystalline anisotropy (MCA) of magnetic materials [1–3]. This is useful for the understanding of permanent magnetic properties, domain wall structure, magnetic nanostructures, etc. One aspect, however, which has received scant attention from such *ab initio* theories is its temperature dependence. Modeling this phenomenon seems to rest largely on the seminal papers by Callen and Callen and others [4] published nearly 40 years ago which focused on the temperature dependence associated with single-ion magnetic anisotropies. In this Letter we investigate how far this approach can be justified for metallic magnets on the basis of a first-principles, material specific, parameter-free theory of how the magnetocrystalline anisotropy depends on temperature. We find that our *ab initio* theory gives the correct behavior of the MCA for a case where the single-ion model fails. The theory involves a detailed, relativistic description of the electronic structure and hence includes a complete description of the spin-orbit coupling. The thermally induced magnetic fluctuations are accounted for by a relativistic generalization of the, by now well-tried, disordered local moment (DLM) picture [5,6].

The topic has recently received extra impetus from extensive experimental studies of magnetic films and nanostructures and their technological potential. For example, the fabrication of assemblies of smaller and smaller magnetic nanoparticles holds considerable promise for the design of ultrahigh density magnetic data storage media [7]. But this is hampered by a particle size limit set so that thermally driven demagnetization and loss of data are avoided over a reasonable storage period. This limit can be lowered by using materials with high magnetocrystalline anisotropy, $K$, since the superparamagnetic diameter of a magnetic particle is proportional to $(k_B T/K)^{1/3}$, where $k_B T$ is the thermal energy [8]. In this context, the chemically ordered $L1_0$ phase of equiatomic FePt, which has high uniaxial MCA ($4–10 \times 10^7$ ergs/cm$^3$ or up to 1.76 meV per FePt pair [9,10]), has attracted much attention and arrays of FePt nanoparticles with diameters as small as 3 nm have been synthesised [7,11]. For a uniaxial magnet like this, $K$ is the difference between the free energies $F^{(0,0,1)}$ and $F^{(1,0,0)}$ of the system magnetized along $(0, 0, 1)$ and $(1, 0, 0)$ crystallographic directions. A way to write to media of very high $K$ material is by temporary heating [12,13]. The MCA is reduced during the magnetic write process and the information is locked in as the material cools. Modeling this process and improving the design of high density magnetic recording media therefore requires an understanding of how $K$ varies with temperature. So for the first application of our theory we have chosen FePt. Given its technological potential there have recently been some careful experimental studies of its fundamental magnetic properties [11,12,14]. These show a strong temperature dependence to $K$. We find good agreement with these data. In particular, we find $K(T) \propto [M(T)/M(0)]^2$ over a broad magnetization range, in line with experimental reports [12,14]. Notably the low temperature behavior is qualitatively different from that of the single-ion anisotropy models used over many years [4].

The MCA of a material can be conveniently expressed as $K = \sum_\gamma k_\gamma g_\gamma(\hat{n})$, where the $k_\gamma$'s are coefficients, $\hat{n}$ is the magnetization direction, and $g_\gamma$'s are polynomials (spherical harmonics) of the angles $\theta$, $\phi$ fixing the orientation of $\hat{n}$ and belong to the fully symmetric representation of the

 

crystal point group. For a uniaxial ferromagnet $K = k_0 + k_2(\cos^2\theta - 1/3) + \cdots$. As the temperature rises, $K$ decreases rapidly. The key features of the results of the early theoretical work on this effect [4] are revealed by a classical spin model pertinent to magnets with localized magnetic moments. The anisotropic behavior of a set of localized ''spins'' associated with ions sitting on crystalline sites, $i$, in the material is given by a term in the Hamiltonian $H_{an} = \sum_i \sum_\gamma k_\gamma g_\gamma(\hat{s}_i)$ with $\hat{s}_i$ a unit vector denoting the spin direction on site $i$. As the temperature is raised, the spins sample the energy surface over a small angular range about the magnetization direction and the anisotropy energy is given from the difference between averages taken for the magnetization along the easy and hard directions. If the coefficients $k_\gamma$ are assumed to be rather insensitive to temperature, the dominant thermal variation of $K$ for a ferromagnet is given by $K(T)/K(0) = \langle g_l(\hat{s})\rangle_T / \langle g_l(\hat{s})\rangle_0$. The averages $\langle\cdots\rangle_T$ are taken such that $\langle\hat{s}\rangle_T = M(T)$, the magnetization of the system at temperature $T$, and $l$ is the order of the spherical harmonic describing the angular dependence of the local anisotropy, i.e., $l = 2$ and 4 for uniaxial and cubic systems, respectively. At low temperatures $K(T)/K(0) \approx [M(T)/M(0)]^{l(l+1)/2}$ and near the Curie temperature $T_c$, $K(T)/K(0) \approx [M(T)/M(0)]^l$. These features are borne out rather well in magnets where the magnetic moments are well localized, e.g., rare-earth and oxide magnets, but it is questionable whether such an analysis should hold for itinerant ferromagnets [8]. Here, we examine FePt for which careful experiments [12,14] find $K(T)/K(0) = [M(T)/M(0)]^n$, where $n = 2$ instead of $n = 3$, over a large temperature range. As we show presently, our *ab initio* calculations are in good agreement with this surprising result.

Magnetocrystalline anisotropy is caused largely by spin-orbit coupling and receives an *ab initio* description from the relativistic generalization of spin density functional theory (SDFT) [1]. Up to now calculations of the anisotropy constants $K$ have been suited to $T = 0$ K only. They treat spin-orbit coupling effects using either perturbation theory [3] or a fully relativistic one [2,15]. Typically the total energy, or the single-electron contribution to it, is calculated for two or more magnetization directions $\hat{n}_1$ and $\hat{n}_2$ separately and then the MCA is obtained from the difference (often of the order of $\mu$eV) [15], $\Delta E = -\int^{E_{F_1}} [N(\varepsilon;\hat{n}_1) - N(\varepsilon;\hat{n}_2)]d\varepsilon - \frac{1}{2}n(E_{F_2};\hat{n}_2)\times (E_{F_1} - E_{F_2})^2 + \mathcal{O}(E_{F_1} - E_{F_2})^3$, where $E_F^1$, $E_F^2$ are the Fermi energies when the system is magnetized along $\hat{n}_1$ and $\hat{n}_2$ and $n(\varepsilon;\hat{n})$ and $N(\varepsilon;\hat{n})$ are the density of states (DOS) and integrated DOS, respectively. We have used this rationale with a fully relativistic theory to study the MCA of magnetically soft, compositionally disordered binary and ternary component alloys [15,16] and the effect upon it of short-range [2] and long-range chemical order [17].

Our MCA calculations use spin-polarized, relativistic multiple scattering theory and an adaptive mesh algorithm for Brillouin zone integrations such that the numerical precision is to within 0.1 $\mu$eV [2,15]. These attributes are also important for the theoretical calculations of the temperature dependence of the MCA described below. We calculate the MCA of ordered FePt at $T = 0$ K to be 1.696 meV. We start from a self-consistent field (SCF), scalar-relativistic calculation (atomic sphere approximation) of the electronic structure and effective potentials for the Fe and Pt sites. We then perform a further fully relativistic electronic structure calculation, recalculate the Fermi energies $E_F^1$ and $E_F^2$, and determine the MCA. There are a number of calculated values of the MCA of completely $L1_0$-ordered FePt at $T = 0$ K in the literature [18] ranging from 1.2 to 3.9 meV per cell ($7–22 \times 10^7$ ergs/cm$^3$). The easy axis as in experiment [9,10] is along the $c$ axis, (0, 0, 1), perpendicular to the Fe and Pt layers. For ordered FePt we find that the large difference in the DOS $[n(E_F^1;\hat{n}_1) - n(E_F^2;\hat{n}_2)]$ at the Fermi energy induces a significant sensitivity of the MCA to the positions of $E_F^1$ and $E_F^2$. For example, the MCA jumps from 1.696 to 2.751 meV if the $E_F$'s are both lowered by 0.2 eV. This sensitivity may explain, in part, the range of published values of the MCA of FePt. We also deduce that the magnetic anisotropy might be further enhanced by replacing a few atomic percent of Pt with Ir.

In a metallic ferromagnet at $T = 0$ K the electronic structure is spin polarized. With increasing temperature, spin fluctuations are induced which eventually destroy the long-range magnetic order and hence the overall spin polarization of the system's electronic structure. These collective electron modes interact as $T$ is raised and are dependent upon and affect the underlying electronic structure. For many materials the magnetic excitations can be modeled by associating local spin-polarization axes with all lattice sites and the orientations $\{\hat{e}_i\}$ vary very slowly on the time scale of the electronic motions [5]. These ''local moment'' degrees of freedom produce local magnetic fields on the lattice sites which affect the electronic motions and are self-consistently maintained by them. By taking ensemble averages over the orientational configurations, the system's magnetic properties can be determined and, with the explicit inclusion of relativistic effects upon the electronic structure, the temperature dependence of its MCA obtained.

Consider this DLM picture of a ferromagnetic metal magnetized along a direction $\hat{n}$ at a temperature $T$. The probability that the system's local moments are configured according to $\{\hat{e}_i\}$ is $P^{(\hat{n})}(\{\hat{e}_i\}) = \exp[-\beta\Omega^{(\hat{n})}(\{\hat{e}_i\})]/Z^{(\hat{n})}$, where the partition function $Z^{(\hat{n})} = \prod_j \int d\hat{e}_j \times \exp[-\beta\Omega^{(\hat{n})}(\{\hat{e}_i\})]$. $\Omega^{(\hat{n})}(\{\hat{e}_i\})$ is the ''generalized'' electronic grand potential from SDFT [6] and $\beta = (k_B T)^{-1}$. The thermodynamic free energy is given by $F^{(\hat{n})} = -k_B T \log Z^{(\hat{n})}$. The role of a local moment Hamiltonian, albeit a highly complicated one, is played by $\Omega\{\hat{e}_i\}$. Expanding about a suitable reference ''spin'' Hamiltonian $\Omega_0\{\hat{e}_i\} = \sum_i h^{(\hat{n})}\hat{n}\cdot\hat{e}_i$ and, using the Feynman inequality [19], gives a mean field theoretical estimate of the free

energy [6].

$$F^{(\hat{n})} = \langle \Omega^{(\hat{n})} \rangle + (1/\beta) \sum_i \int P^{(\hat{n})}(\hat{e}_i) \ln P^{(\hat{n})}(\hat{e}_i) d\hat{e}_i, \quad (1)$$

where the probability distribution is

$$P^{(\hat{n})}(\hat{e}_i) = \frac{\exp[-\beta h^{(\hat{n})} \hat{n} \cdot \hat{e}_i]}{\int \exp[-\beta h^{(\hat{n})} \hat{n} \cdot \hat{e}_i] d\hat{e}_i} \quad (2)$$

and the Weiss field at a site is given by

$$h^{(\hat{n})} = \frac{3}{4\pi} \int \langle \Omega^{(\hat{n})} \{\hat{e}_l\} \rangle_{\hat{e}_i} \hat{n} \cdot \hat{e}_i d\hat{e}_i, \quad (3)$$

where $\langle \cdots \rangle_{\hat{e}_i}$ denotes a constrained statistical average with the moment on site $i$ being fixed along $\hat{e}_i$. The choice of the reference Hamiltonian $\Omega_0\{\hat{e}_i\}$ as a sum of the interactions of Weiss field $h^{(\hat{n})}\hat{n}$ with local moments $\hat{e}_i$ on each site means that a mean field description of the ferromagnetic system magnetized along $\hat{n}$ is constructed with no reference to an external field.

The magnetization $\mathbf{M} = M\hat{n}$ is given by $M = \mu \int P^{(\hat{n})}(\hat{e}_i) \hat{n} \cdot \hat{e}_i d\hat{e}_i$. $\mu$ is the size of the local moment on the site and is determined self-consistently [6]. The DLM picture is well justified for materials in which the sizes of the local moments, $\mu$, remain fairly constant so that even in the paramagnetic state where $M = 0$, the $\mu$'s are roughly the same as the magnetic moment per atom in the ferromagnetic state at $T = 0$ K. In a first-principles implementation of the DLM picture, the averaging over the orientational configurations of the local moments is performed using techniques adopted from the theory of random metallic alloys [6,20]. Over the past 20 years, the paramagnetic state, the onset of magnetic order, and transition temperatures of many systems have been successfully described [21]. All applications to date, however, have neglected relativistic effects and have been devoted to the paramagnetic state where the symmetry turns the calculation into a binary alloy-type one with half the moments oriented along a direction and the rest antiparallel. Once relativistic effects are included and/or the ferromagnetic state is considered, this simplicity is lost and the continuous probability distribution $P^{(\hat{n})}(\hat{e}_i)$'s must be sampled for a fine mesh of angles and the averages with the probability distribution performed numerically. (Careful checks have to be made to ensure that the sampling of $P^{(\hat{n})}(\hat{e}_i)$ is sufficient—we use some 25 000 values.) In the ferromagnetic state, the magnetic anisotropy is given by the difference between the free energies $F^{(\hat{n})}$ for different magnetization directions $\hat{n}$, but the same magnetization $M$.

Once again our study of FePt starts with a SCF, scalar-relativistic calculation, this time for the paramagnetic (DLM) state. On the Fe sites a local moment of $2.97\mu_B$ is set up while no moment forms on the Pt sites. For the same lattice spacings ($c = 0.385$ nm, $c/a = 1$), we found that, for the completely ferromagnetically ordered state of FePt at $T = 0$ K, the magnetization per Fe site is $2.93\mu_B$ and a small magnetization of $0.29\mu_B$ is associated with the Pt sites. This suggests that the thermal effects on the magnetic properties should be well described by the DLM picture (see the previous paragraph). Using the self-consistent potentials and effective fields of the paramagnetic DLM state, we proceed, using a simple trick to avoid an iterative determination of the Weiss field [Eqs. (2) and (3)] for a given temperature $T$, by picking a series of values of $\lambda (= \beta h^{(\hat{n})})$ to set the probabilities, $P^{(\hat{n})}(\hat{e}_i)$ (and magnetizations $M$). A calculation of $\langle \Omega^{(\hat{n})} \{\hat{e}_l\} \rangle_{\hat{e}_i}$ [Eq. (3)] gives the Weiss field $h^{\hat{n}}$. The ratio of $h^{\hat{n}}$ to $\lambda$ then uniquely determines the temperature $T$ for each of the initially chosen values of $\lambda$ and hence $M(T)$. The results are shown in Fig. 1. Although the shortcomings of the mean field approach do not produce the spin wave $T^{3/2}$ behavior at low temperatures, the easy axis for the onset of magnetic order is obtained ($h^{(001)} > h^{(100)}$ as $T \to T_c$), and it corresponds to that found at lower temperatures both experimentally and in all theoretical ($T = 0$ K) calculations. (An adaptation to systems such as thin films combined with $T = 0$ K calculations may be useful in understanding temperature induced spin reorientation transitions.) $T_c = 935$ K, in fair agreement with the experimental value of 750 K [6]. (An Onsager cavity field technique would improve this estimate, see [6], without affecting the quality of the following results.)

The free energy difference, $F^{(0,0,1)} - F^{(1,0,0)}$, i.e., the MCA, $K(T)$, is calculated using the theory and leads to the key results of this Letter shown in Fig. 2. At $T = 0$ K, the MCA has a value $-1.740$ meV, close to the value, $-1.696$ meV, obtained by the earlier, separate calculation for the completely ferromagnetic state. As $T$ is raised the

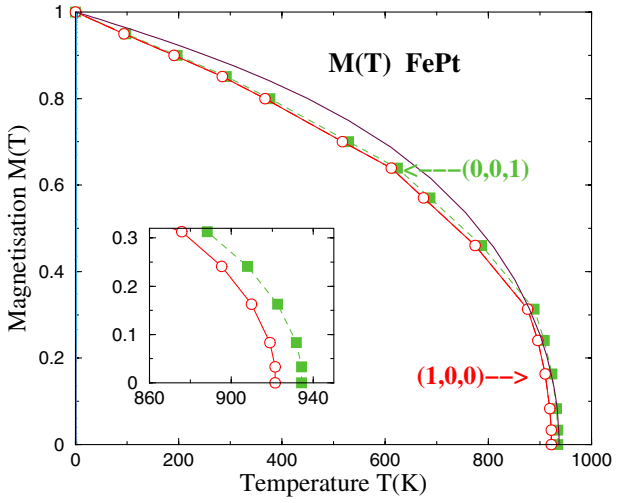


FIG. 1 (color online). The magnetization of FePt versus $T$. The filled squares refer to a magnetization along (0, 0, 1) and the open circles along (1, 0, 0). $T_c$ is at 935 K with the easy axis, (0, 0, 1). The full line shows the mean field approximation to a classical Heisenberg model for comparison. In the inset, near $T_c$, the lower intercept shows what $T_c$ would be with the system constrained to become magnetically ordered along (1, 0, 0).

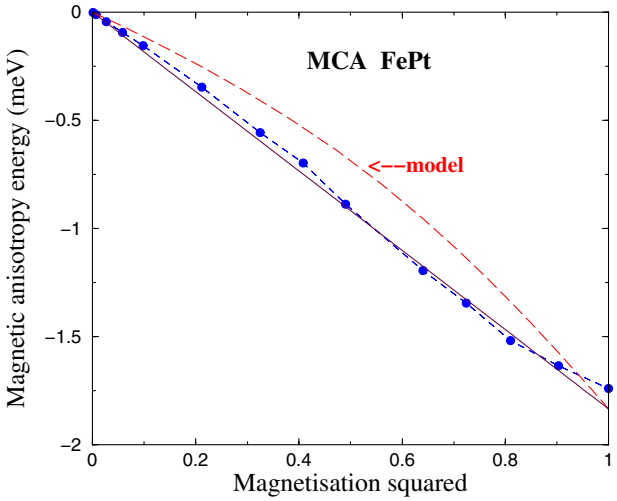


FIG. 2 (color online). The magnetic anisotropy of FePt as a function of the square of magnetization. The filled circles show the calculations from the *ab initio* theory, the full line $K_0[M(T)/M(0)]^2$, and the dashed line the single-ion model function $K_0\langle g_2(\hat{e})\rangle_T/\langle g_2(\hat{e})\rangle_0$ with $K_0 = -1.835$ meV.

statistical fluctuations of the orientations of the local moments, which cause the magnetization $M$ to drop, make $K$ vary markedly with $T$ and to be a function of $M$. Figure 2 shows $K(T)$ versus $[M(T)/M(0)]^2$ together with a curve for the single-ion classical spin model anisotropy [4] for comparison. Apart from $0.9 < M(T)/M(0) < 1$ our results show an approximate $[M(T)/M(0)]^2$ behavior in good agreement with experiment [12,14]. This is in marked contrast to the model, which becomes proportional to $[M(T)/M(0)]^3$ for the larger $M(T)$'s.

Evidently Fig. 2 shows that at low temperatures in the single-ion model the MCA falls off much more quickly as the temperature is increased and the overall magnetization is reduced. Moreover, our itinerant electron theory does capture the behavior of the $K$ versus magnetization relation quantitatively. This theory assumes that there is a separation between fast and slow electronic degrees of freedom. A picture of ''local moments'' emerges naturally but with a subtlety that their existence and behavior are determined by the fast electronic motions. It also assumes that rigid coupling between neighboring local moments is readily destroyed by thermal fluctuations. For this uncorrelated regime, considerations similar to those applied to simple spin models by Callen and Callen [4] may suggest the basis for the $M^2$ dependence of the MCA we find here. We expect the MCA of the important magnetic materials $L1_0$-CoPt and FePd to follow a similar variation with magnetization since the local moments sustained on the Co and Fe sites in the paramagnetic DLM states ($1.78\mu_B$ and $2.98\mu_B$, respectively) are comparable in size to magnetization per site in the completely ferromagnetic states ($1.91\mu_B$ and $2.96\mu_B$). Our DLM theory therefore has good prospects in describing the variation of $K$ with magnetization for a range of such metallic magnets. The success of the above relativistic DLM methodology in explaining the unexpected behavior of $L1_0$-FePt suggests that further calculations for promising magnetic materials in bulk, thin films, or in magnetic nanostructures may be valuable for the future modeling and exploitation of their magnetic properties.

We acknowledge support from the EPSRC (U.K), CSAR, the CSC at the University of Warwick, and the Hungarian NSF (OKTA T046267).

[1] H. J. F. Jansen, Phys. Rev. B **59**, 4699 (1999).
[2] S. S. A. Razee *et al.*, Phys. Rev. Lett. **82**, 5369 (1999).
[3] For example, T. Burkert *et al.*, Phys. Rev. B **69**, 104426 (2004); A. B. Shick *et al.*, Phys. Rev. B **56**, R14 259 (1997).
[4] H. B. Callen and E. Callen, J. Phys. Chem. Solids **27**, 1271 (1966); N. Akulov, Z. Phys. **100**, 197 (1936); C. Zener, Phys. Rev. **96**, 1335 (1954).
[5] *Electron Correlations and Magnetism in Narrow Band System*, edited by T. Moriya (Springer, New York, 1981).
[6] J. B. Staunton and B. L. Gyorffy, Phys. Rev. Lett. **69**, 371 (1992); B. L. Gyorffy *et al.*, J. Phys. F **15**, 1337 (1985).
[7] S. Sun *et al.*, Science **287**, 1989 (2000).
[8] R. C. O'Handley, *Modern Magnetic Materials* (Wiley, New York, 2000).
[9] T. Klemmer *et al.*, Scr. Metall. Mater. **33**, 1793 (1995).
[10] R. F. Farrow *et al.*, J. Appl. Phys. **79**, 5967 (1996).
[11] X. W. Wu *et al.*, Appl. Phys. Lett. **82**, 3475 (2003).
[12] J.-U. Thiele *et al.*, J. Appl. Phys. **91**, 6595 (2002).
[13] A. Lyberatos and K. Y. Guslienko, J. Appl. Phys. **94**, 1119 (2003); H. Saga *et al.*, Jpn. J. Appl. Phys., Part 1 **38**, 1839 (1999); M. Alex *et al.*, IEEE Trans. Magn. **37**, 1244 (2001).
[14] S. Okamoto *et al.*, Phys. Rev. B **66**, 024413 (2002).
[15] S. S. A. Razee *et al.*, Phys. Rev. B **56**, 8082 (1997).
[16] S. Ostanin *et al.*, Phys. Rev. B **69**, 064425 (2004).
[17] J. B. Staunton *et al.*, J. Phys. Condens. Matter **16**, S5623 (2004).
[18] G. H. O. Daalderop *et al.*, Phys. Rev. B **44**, 12 054 (1991); I. V. Solovyev *et al.*, Phys. Rev. B **52**, 13 419 (1995); I. Galanakis *et al.*, Phys. Rev. B **62**, 6475 (2000); P. Ravindran *et al.*, Phys. Rev. B **63**, 144409 (2001); S. D. Willoughby *et al.*, J. Appl. Phys. **91**, 8822 (2002); A. B. Shick and O. N. Mryasov, Phys. Rev. B **67**, 172407 (2003).
[19] R. P. Feynman, Phys. Rev. **97**, 660 (1955).
[20] G. M. Stocks and H. Winter, Z. Phys. B **46**, 95 (1982); D. D. Johnson *et al.*, Phys. Rev. Lett. **56**, 2088 (1986).
[21] For example, M. F. Ling *et al.*, Europhys. Lett. **25**, 631 (1994); S. S. A. Razee *et al.*, Phys. Rev. Lett. **88**, 147201 (2002); A. M. N. Niklasson *et al.*, Phys. Rev. B **67**, 235105 (2003).