Dynamics of the Peierls-active phonon modes in $CuGeO_3$

Claudius Gros and Ralph Werner
Institut für Physik, Universität Dortmund, D-44221 Dortmund, Germany
(Received 12 August 1998)

We reconsider the Cross and Fischer approach to spin-Peierls transitions. We show that a soft phonon occurs only if $\Omega_0 < 2.2 T_{SP}$. For $CuGeO_3$ this condition is not fulfilled and the calculated temperature dependence of the Peierls-active phonon modes is in excellent agreement with experiment. A central peak of a width ~ 0.2 meV is predicted at T_{SP}. Good agreement is found between theory and experiment for the pretransitional Peierls fluctuations. Finally, we consider the problem of quantum criticality in $CuGeO_3$. [S0163-1829(98)51046-6]

Structural phase transitions come essentially in two varieties, those with a soft phonon mode and those without phonon softening and a central peak.[1] Typically one associates them to displacive and to order-disorder transitions, respectively, even though there is no strict formal distinction between displacive and order-disorder transitions. It came then as a surprise that the spin-Peierls transition in $CuGeO_3$,[2] which had been shown to be displacive,[3] shows no phonon softening.[3,4] Even worse, the Peierls-active phonon modes harden by about 5–6 % with decreasing temperature.[5] It has been generally assumed, up to now, that this behavior is inconsistent with the random-phase approximation (RPA) approach by Cross and Fischer (CF) to the spin-Peierls transition.[6] Here we show that the CF theory is actually fully consistent with the experimental results for $CuGeO_3$. We show that soft phonons occur within RPA only if the bare phonon frequency Ω_0 satisfies $\Omega_0 < 2.2 T_{SP}$. For larger phonon frequencies the phonon does not soften and a central peak develops at the spin-Peierls transition temperature T_{SP}. We then test the applicability of RPA to $CuGeO_3$ by calculating the pretransitional Peierls fluctuations. We find good agreement with experiment. Finally, we note that a key ingredient of the CF approach, quantum criticality, can be tested for in $CuGeO_3$.

RPA approach. The retarded phonon Green's function $D_q(\omega)$ is given by[7]

$$D_q(\omega) = \frac{2\Omega_0(q)}{\omega^2 - \Omega_0^2(q) - 2\Omega_0(q) P_q(\omega)}, \tag{1}$$

where $\Omega_0(q)$ is the frequency of the bare phonon with momentum q. In RPA one approximates the phonon self-energy $P_q(\omega)$ by $g_q^2 \chi_q(\omega)$, where $\chi_q(\omega)$ is the dynamical energy-energy correlation function and where g_q is the electron-phonon coupling constant, given by

$$|g_q|^2 = \frac{\lambda^2 \hbar}{M \Omega_0(q)} (1 - \cos(qc)), \tag{2}$$

where we have used

$$\sum_n \lambda (u_{n+1} - u_n) \mathbf{S}_n \cdot \mathbf{S}_{n+1}, \tag{3}$$

for the spin-phonon coupling within a linear-chain model. Here $\mathbf{S}_n$ are the spin operators at site n, u_n the displacement operators for the normal coordinates of the Peierls-active phonon mode,[5,8] and M is the effective mass of the normal mode.

At the spin-Peierls transition a spontaneous dimerization occurs below T_{SP}, at $q = \pi/c$. In the following we set the lattice constant c to unity in the theory formulas. Cross and Fischer observed that the correct functional form for $\chi_q(\omega)$ (in the limit $\omega \to 0$) can be obtained from bosonization,[6]

$$T \chi_q(\omega) = -2 d I_1\left(\frac{\omega - \Delta}{2\pi T}\right) I_1\left(\frac{\omega + \Delta}{2\pi T}\right), \tag{4}$$

where $d \approx 0.37$ is a constant depending weakly on the momentum cutoff, $\Delta = v_s |q - \pi|$ is the lower edge of the two-spinon continuum (v_s is the renormalized spin-wave velocity), and

$$I_1(k) = \frac{1}{2\pi} \int_0^\infty dx\, e^{ikx} (\sinh(x))^{-1/2}.$$

$T\chi_{q=\pi}(\omega)$ is scale invariant and a function of $\omega/(2\pi T)$ only (independent of the spin-spin coupling J). This behavior is characteristic of quantum critical systems.[9] For any temperature $T > 0$ we can expand $T\chi_\pi(\omega)$ in $\omega/(2\pi T)$ as

$$T \chi_\pi(\omega) = -\chi_0 - i \chi_1 \left(\frac{\omega}{2\pi T}\right) + \chi_2 \left(\frac{\omega}{2\pi T}\right)^2 + \cdots, \tag{5}$$

with $\chi_0 \approx 0.26$, $\chi_1 \approx 0.81$, and $\chi_2 \approx 2.2$. The position of the poles ω_π of $D_\pi(\omega)$ are then determined by the roots of

$$\frac{\omega^2 - \Omega_0^2}{2\Omega_0 g_\pi^2} = \mathrm{Re}\, \chi_\pi(\omega) \approx -\frac{\chi_0}{T} + \frac{\chi_2}{T} \left(\frac{\omega}{2\pi T}\right)^2, \tag{6}$$

where $\Omega_0 \equiv \Omega_0(\pi)$. Typical plots of the left- and right-hand side (rhs) of Eq. (6) are presented in Fig. 1.

A spontaneous lattice dimerization, i.e., a macroscopic occupation of the Peierls-active phonon mode, occurs at T_{SP} when Eq. (6) has a solution for $\omega = 0$. This determines the transition temperature as[6]

$$T_{SP} = \frac{2 g_\pi^2}{\Omega_0} \chi_0. \tag{7}$$

0163-1829/98/58(22)/14677(4)/$15.00

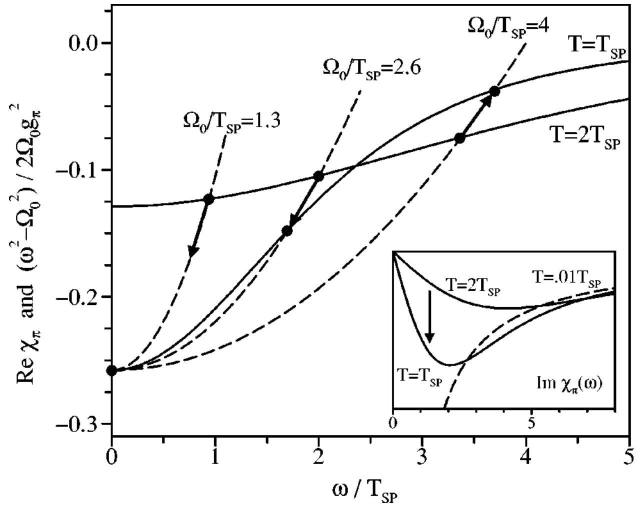

FIG. 1. Plots of Re $\chi_\pi(\omega)$ (solid lines) for $T=T_{SP}$ and $T=2T_{SP}$, as a function of ω/T_{SP}. The temperature independent left-hand side (lhs) of Eq. (6), $(\omega^2-\Omega_0^2)/(2\Omega_0 g_\pi^2)$, is plotted for $\Omega_0/T_{SP}=1.3,2.6,4$ (dashed lines), with g_π given by Eq. (7). The filled circles denote the position of the phonon frequencies ω_π. The arrows indicate the shift of ω_π with decreasing temperature. Inset: Im $\chi_\pi(\omega)$.

Remarkably, Eq. (7) is independent of J, due to the scale invariance of $T\chi_\pi(\omega)$. We compare the prefactor of the terms $\sim\omega^2$ of the rhs and lhs of Eq. (6) and find that for

$$1/(2g_\pi^2\Omega_0)>\chi_2/(4\pi^2T_{SP}^3), \tag{8}$$

Eq. (6) has a single solution for $T=T_{SP}$ and inspection of the temperature dependence of this solution for $T>T_{SP}$ [compare Fig. (1)] shows that this root continuously connects to the $T=\infty$ solution, $\lim_{T\to\infty}\omega_\pi=\Omega_0(\pi)$. In the parameter regime defined by Eq. (8) the phonon softens completely. We can use Eq. (7) to eliminate g_π from Eq. (8). We obtain

$$T_{SP}>\frac{\Omega_0}{2\pi}\sqrt{\frac{\chi_2}{\chi_0}}\approx 0.46\Omega_0, \quad \Omega_0<2.2T_{SP}, \tag{9}$$

for the soft-phonon regime. For $\Omega_0>2.2T_{SP}$ the Peierls-active phonon does not soften completely and may even become harder with decreasing temperature, as illustrated in Fig. 2. Near $T=T_{SP}$ an additional central peak shows up, leading to the phase transition. For $CuGeO_3$ there are two Peierls-active phonon modes with energies[5] $\omega_1=151$ K and $\omega_2=317$ K, respectively. Since (see below) $\Omega_\gamma\approx\omega_\gamma$ ($\gamma=1,2$) and $T_{SP}=14.1$ K we find that $CuGeO_3$ is in the central-peak regime.

Application to $CuGeO_3$. In order to compare more in detail with the experimental results for $CuGeO_3$ we have generalized Eq. (1) for the case of two phonon frequencies. Denoting by $D_{1/2}(\omega)$ the retarded Green's functions of the first and second phonon with bare frequencies Ω_1 and Ω_2, respectively, and by g_1 and g_2 the respective spin-phonon coupling constants, we obtain

$$D_1(\omega)=D_1^{(0)}(\omega)+\frac{(D_1^{(0)}(\omega))^2g_1^2\chi_\pi(\omega)}{1-(g_1^2D_1^{(0)}(\omega)+g_2^2D_2^{(0)}(\omega))\chi_\pi(\omega)}$$

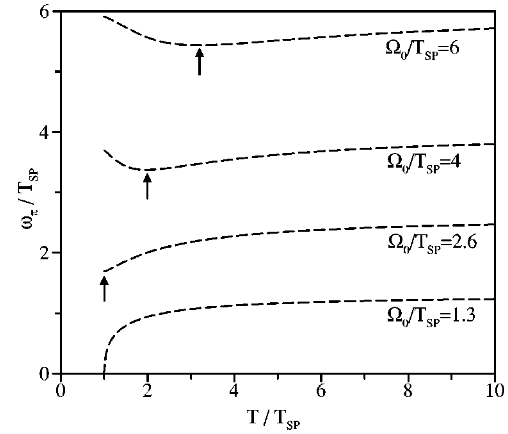

FIG. 2. The temperature dependence of the phonon frequencies ω_π for various values of Ω_0/T_{SP}. Ω_0 is the bare phonon frequency. The arrows indicate the respective minimal phonon frequency.

and an equivalent equation for $D_2(\omega)$. Here $D_{1/2}^{(0)}(\omega)=2\Omega_{1/2}/(\omega^2-\Omega_{1/2}^2)$.[7] An analysis similar to the one-phonon case can be performed for $D_1(\omega)+D_2(\omega)$. One finds

$$T_{SP}=\left(\frac{2g_1^2}{\Omega_1}+\frac{2g_2^2}{\Omega_2}\right)\chi_0 \tag{10}$$

for the transition temperature and

$$T_{SP}>\sqrt{\frac{\chi_2}{\chi_0}}\frac{\Omega_1\Omega_2}{2\pi}\sqrt{\frac{g_1^2\Omega_2+g_2^2\Omega_1}{g_1^2\Omega_2^3+g_2^2\Omega_1^3}} \tag{11}$$

for the soft-phonon regime.

In order to determine g_1 and g_2 for $CuGeO_3$ we note that the lower/upper phonon mode contributes to the structural distortion below T_{SP} with weighting factors 2 and 3, respectively.[5] This leads to

$$\frac{g_1/\sqrt{\Omega_1^3}}{g_2/\sqrt{\Omega_2^3}}=\frac{2}{3}, \quad \frac{g_1}{g_2}=\frac{2\sqrt{\Omega_1^3}}{3\sqrt{\Omega_2^3}}\approx\frac{2\sqrt{\omega_1^3}}{3\sqrt{\omega_2^3}}\approx\frac{1}{4}. \tag{12}$$

Equations (12) and (10) determine the spin-phonon couplings g_1,g_2. For $T_{SP}=14.1$ K we find $\Omega_1=3.13$ THz and $\Omega_2=6.65$ THz for the bare phonon frequencies and $g_1=0.45$ THz ($g_2=4g_1$) for the spin-phonon coupling.

In Fig. 3 we have plotted the results for the dynamical structure factor,

$$S(\pi,\omega)=-\frac{1}{\pi}\frac{\mathrm{Im}[D_1(\omega+i\delta)+D_2(\omega+i\delta)]}{1-\exp(-\beta\omega)}, \tag{13}$$

where we have used the experimental resolution function [THz] $\delta\approx 0.023+0.028\omega/(2\pi)$.[10] The intensity of the experimental spectra,[5] also shown in Fig. 3, has been scaled; the (constant) background has been adjusted.[11] The overall agreement between experiment and theory is satisfactory, although the hardening of the lower phonon mode is somewhat more pronounced in the experiment (6% vs 1%). No experimental data for the upper mode were available for $T=16$ K. In the inset a blowup of the central peak is given. It should be possible to resolve the predicted central peak below $\sim$20 K. It has a width of $\approx$0.05 THz=0.2 meV.

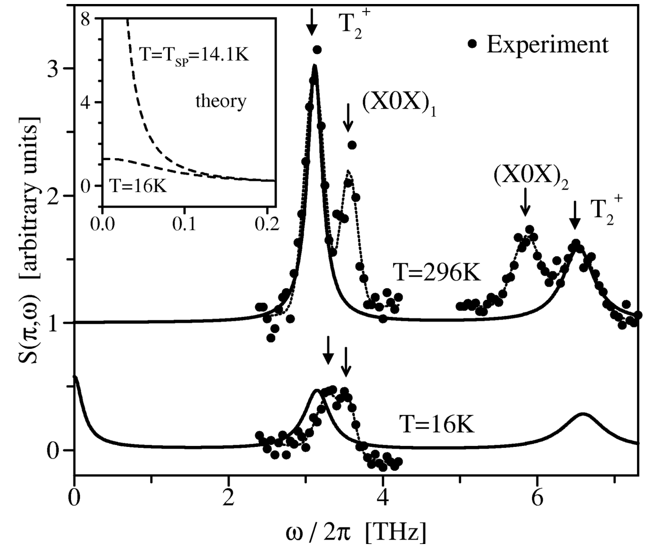

FIG. 3. Theoretical (thick solid lines) and experimental (solid circles, Ref. 5) results for the dynamical structure factor. The T_2^+ phonons are Peierls active and included in the theory, $(XOX)_1$ and $(XOX)_2$ are other nearby phonons. The data for $T=296$ K have been shifted. Inset: Blowup of the central peak at $T=T_{SP}=14.1$ K and $T=16$ K (not broadened).

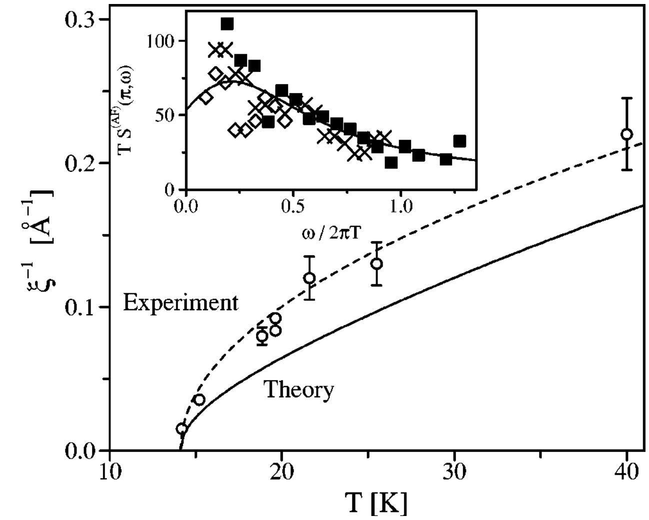

FIG. 4. RPA and experimental results (Ref. 16) for the inverse lattice correlation length $1/\xi$. The theory does not contain any free parameter. Inset: $TS^{(AF)}(\pi,\omega)$, as a function of $\omega/(2\pi T)$, as predicted by bosonization [solid line, Eq. (4)], and the neutron-scattering results,[3] for $T=14.5$ K (filled squares), $T=20$ K (crosses), and $T=50$ K (diamonds).

The theory presented here is based on the RPA approximation. Cross and Fischer[6] have shown that corrections to RPA are small whenever the Peierls-active phonon modes are already soft far above T_{SP}. Here ''soft'' means soft relative to the other (non-Peierls active) phonon modes.[17] This condition is not fulfilled for $CuGeO_3$ and one might question the applicability of RPA in the central-peak regime. In view of the fact that standard phenomenological theories for the central peak occurring in structural phase transitions have RPA form,[1] one might reasonably expect that corrections to RPA do not change the results presented here qualitatively. In order to estimate the (quantitative) magnitude of the corrections to RPA for $CuGeO_3$ we have compared the RPA prediction for inverse lattice correlation length $1/\xi$ with the experimental pretransitional Peierls fluctuations.

The lattice correlation length is determined by the long-distance falloff,

$$\lim_{z\to\infty}\int\frac{dq}{2\pi}\,e^{iqz}\mathrm{Re}\,D_q(0)\sim e^{i\pi z/c}e^{-z/\xi}, \tag{14}$$

where $c=2.94$ Å is the c axis lattice constant of $CuGeO_3$ and $D_q(\omega)=\Sigma_\gamma D_{q,\gamma}(\omega)$. We have calculated $1/\xi$ from Eq. (14), using $v_s=(\pi/2)J(1-1.12\alpha)$ (Ref. 12) [which enters Eq. (4)], $J=156$ K for the exchange integral, and $\alpha=0.24$ for the frustration parameter.[13–15] The results for $1/\xi$ are presented in Fig. 4, together with results for $CuGeO_3$ obtained by diffusive x-ray scattering,[16] which are consistent with neutron-scattering data and the absence of a soft phonon.[3]

Both experiment and theory show mean-field behavior, $1/\xi\sim\sqrt{T-T_{SP}}$. The RPA result agrees well with experiments. Above $T=19$ K the lattice fluctuations have one-dimensional character[16] and the residual difference between theory and experiment may be due to corrections to RPA.

It is interesting to note that Eq. (4) for $\chi_q(\omega)$ is (for spin-rotational invariant Heisenberg chains) identical with the bosonization result for the magnetic dynamical structure factor, $S^{(AF)}(q,\omega)$.[18] Quantum criticality implies $TS^{(AF)}(\pi,\omega)$ to be a universal function of $\omega/(2\pi T)$, at least for small ω. In the inset of Fig. 4 we have plotted the bosonization result for $TS^{(AF)}(\pi,\omega)$, together with the rescaled neutron-scattering results.[3] We observe that the experimental data approximately obey the scaling, though there is substantial scattering of the data for small $\omega/(2\pi T)$, possibly influenced by noncritical contributions from the Peierls fluctuations or by a crossover of the character of the magnetic excitations from one to two dimensions near the Peierls transition.[14] It is also interesting to note that the prediction for $TS^{(AF)}(\pi,\omega)$ is independent of J and that the data for other one-dimensional Heisenberg antiferromagnets with very different values of the coupling J, like $KCuF_3$,[19] should fall onto the same universal curve presented in the inset of Fig. 4. An experimental verification of quantum criticality for $S^{(AF)}(\pi,\omega)$ would imply also scale invariance for $\chi_\pi(\omega)$, since both coincide within bosonization.[6,18]

Generalization. Until now we assumed spin-rotational invariance. Next we will show that a central-peak regime occurs also in spin-Peierls transitions lacking spin-rotational invariance. An example is the spin-Peierls transition in a system of phonons coupled to an array of chains with Ising spins. This model was solved exactly by Pytte.[20] It contains a parameter regime, where the transition is displacive and phonons do not become soft. In the oppositive limit, when the spin chains are xy-like, the transition corresponds via the Jordan-Wigner transformation to the standard Peierls transition.[21] Again one can show[22] that soft phonons occur in RPA, e.g., for $T_{SP}=J/10$, only for $\Omega_0<0.8J$. For $\Omega_0>0.8J$ the Peierls-active phonon does not become soft and a central peak arises at T_{SP}.

Discussion. In this paper we have shown that the RPA approach to the spin-Peierls transition includes both a soft-phonon and a central-peak regime. This result is at first sight counterintuitive, as continuous lattice distortions below T_{SP} are generally associated with a softening of the lattice above T_{SP}.

The eigenstates of the spin-phonon system evolve adiabatically as a function of the spin-phonon coupling strength in the soft-phonon regime. In the central-peak regime a new magnetophonon appears at low frequencies and condenses at T_{SP}, leading to the structural transition and the formation of spin singlets. This new collective excitation is a superposition of a phonon with two magnons in a (valence-bond) singlet state. Condensation of this magnetophonon at T_{SP} leads to the simultaneous formation of the valence-bond singlets and the dimerization of the lattice. The magnetophonon couples to the phonon propagator and therefore shows up as a low-energy resonance in $D_q(\omega)$, the central peak. The other resonance in $D_q(\omega)$, at ω_π, has the limit $\lim_{g_\pi\to 0}\omega_\pi =\Omega_0(\pi)$. Therefore one usually regards ω_π to be the ''true'' phonon frequency. In terms of the eigenstates of the coupled spin-phonon system such a distinction does not make sense. In the central-peak regime the spectral weight of $D_q(\omega)$ is divided in between the ''phonon-resonance'' at ω_π and the soft magnetophonon.

Conclusions. The absence of a soft Peierls-active phonon mode in $CuGeO_3$ has been considered as a challenge to theory. It has been argued[23] that the Cross and Fischer theory is essentially incomplete, i.e., not applicable to $CuGeO_3$. Here we point out that the absence of soft phonons does actually find a natural explanation within the CF approach. The calculated temperature dependence of the phonon modes and that of the pretransitional Peierls fluctuations are in excellent agreement with experiment. A central peak of width 0.2 meV is predicted to appear at T_{SP}. Finally, we have pointed out, that a key ingredient of the theory, the quantum criticality of $\chi_\pi(\omega)$, can be tested, albeit indirectly, with neutron scattering through a test of the scale invariance of the magnetic dynamical structure factor $S^{(AF)}(\pi,\omega)$.

We acknowledge discussions with M. Braden, A. Kluemper, U. Löw, V. N. Muthukumar, and W. Weber. We are especially grateful to M. Braden for sending us the data files. The support of the German Science Foundation is acknowledged.

[1] A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor & Francis, London, 1981).
[2] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[3] K. Hirota *et al.*, Phys. Rev. B **52**, 15 412 (1995).
[4] J. E. Lorenzo *et al.*, Phys. Rev. B **50**, 1278 (1994).
[5] M. Braden, B. Hennion, W. Reichardt, D. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **80**, 3634 (1998).
[6] M. C. Cross and D. S. Fischer, Phys. Rev. B **19**, 402 (1979); M. C. Cross, *ibid.* **20**, 4606 (1979).
[7] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1981).
[8] M. Braden *et al.*, Phys. Rev. B **54**, 1105 (1996).
[9] J. A. Hertz, Phys. Rev. B **14**, 1165 (1976).
[10] M. Braden (private communication).
[11] A rough comparsion (Ref. 10) indicates, that the experimental intensity ratio of the lower T_2^+ mode at $T=295$ K and $T=16$ K is about 3:1, in agreement with theory (see Fig. 3).
[12] A. Fledderjohann and C. Gros, Europhys. Lett. **37**, 189 (1997).
[13] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).
[14] V. N. Muthukumar *et al.*, Phys. Rev. B **54**, R9635 (1996).
[15] The exact value of α 0.24−0.35 has not been determined yet; see, e.g., K. Fabricius *et al.*, Phys. Rev. B **57**, 1102 (1998).
[16] J. P. Pouget *et al.*, Phys. Rev. Lett. **72**, 4037 (1994).
[17] This statement is in agreement with the observation that RPA becomes exact for models with a finite number of phonons; see U. Brandt and H. Leschke, Z. Phys. **271**, 295 (1974).
[18] H. J. Schulz, Phys. Rev. B **34**, 6372 (1986).
[19] D. A. Tennat, R. A. Cowley, S. E. Nagler, and A. M. Tsvelik, Phys. Rev. B **52**, 13 368 (1995).
[20] E. Pytte, Phys. Rev. B **10**, 2039 (1974).
[21] M. J. Rice and S. Strässler, Solid State Commun. **13**, 125 (1973).
[22] R. Werner and C. Gros (unpublished).
[23] G. S. Uhrig, Phys. Rev. B **57**, R14 004 (1998).