Anomalous hypersonic behavior of $CuGeO_3$ prior to the spin-Peierls transition

R. J. Jiménez Riobóo, M. García-Hernández, and C. Prieto
Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco s/n, E-28049 Madrid, Spain

J. E. Lorenzo
Laboratoire de Cristallographie du CNRS, BP 166X, F-38042 Grenoble Cedex, France

L. P. Regnault
CEA/Département de Recherche Fondamentale sur la Matière Condensée, Service de Physique Statistique, Magnétisme et Supraconductivité, Laboratoire de Magnétisme et Diffraction Neutronique, Centre d'Etudes Nucléaires, F-38054 Grenoble Cedex 9, France

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The temperature dependence of the longitudinal elastic constants c_{22}, c_{33}, and of the transverse elastic constant c_{44}, as obtained by Brillouin spectroscopy, reveals an unexpected elastic behavior in $CuGeO_3$ prior to the spin-Peierls magnetic transition ($T_{SP} \approx 14.1$ K). At room temperature $c_{33} \gg c_{44} > c_{22}$. Below about 50 K a steep increase in the values of the longitudinal elastic constants leads to a crossover of the values of c_{22} and c_{44} with $c_{22} > c_{44}$. The existence of translation-rotation coupling in $CuGeO_3$ could account for the elastic behavior above T_{SP}. The anisotropy of the magnetoelastic coupling at the spin-Peierls transition temperature is reflected in the different temperature behavior of the elastic constants (c_{33}, c_{44}, and c_{22}) at $T_{SP} \approx 14.1$ K. [S0163-1829(98)00737-1]

INTRODUCTION

The discovery of the compound $CuGeO_3$ has proved to be a touchstone for quantum theories of one-dimensional antiferromagnetic (AF) interactions. Most of the theoretical issues pointed out by theoreticians in the framework of these systems,[1] such as the presence of a nonmagnetic ground state,[2] a spin-lattice coupling, a lattice dimerization,[3] a continuum of magnetic excitations,[4,5] coexistence of magnetic and nonmagnetic ground states[6] in lightly doped samples, etc., seem to be relevant, or at least to play a role in describing the properties of this fascinating compound. Others, such as competing antiferromagnetic exchange interactions,[7,8] or weak spin anisotropy (possibly of antisymmetric origin),[9] which were not foreseen by the theories in the first place, have been added to the scientific wealth of the physics of $CuGeO_3$. Whereas the magnetic state at low temperatures is fairly well understood, the exact origin of the phase transition is still under active debate. Due to the elastic energy contribution a long-range order is reached in the spin-Peierls state, which has been experimentally observed in the temperature dependence of the lattice parameters below the phase transition temperature ($T_{SP} = 14.1$ K).[5,10] The standard belief that the spin-Peierls state, by analogy to the Peierls state in quasi-one-dimensional charge-density-wave materials,[11] is produced by a magnetoelastic coupling between the one-dimensional magnetic fluctuations and a soft phonon mode seems to be at stake, in view of the very recent inelastic-neutron-scattering data,[12] where no soft mode has been observed. On the other hand, magnetic frustration may trigger a spontaneous lattice dimerization without the help of any soft mode.

Braden *et al.*,[13] on the basis of the temperature evolution of the interatomic distances above and below the spin-Peierls transition, realized that there is a progressive and simultaneous rotation of the O(2)-O(2) edges of the octahedron and a rigid translation of the GeO_4 tetrahedron. Under the action of these two rigid-molecule variables, the corresponding volume thermal expansion/reduction experienced by $CuGeO_3$ on cooling is realized mainly in the empty cavities between the octahedron and the tetrahedron. On the contrary, the phase transition induces a rotation of the $GeO(2)_2$ units around the *c* axis, with the neighboring tetrahedra rotated in opposite senses, and an additional displacement of the Cu atoms along the *c* axis. From the point of view of the Cu, the O(2) displacements can be seen as a compound rotation compression (or dilation) of the Cu-O(2) distance in the *a*-*b* plane. Hence one may consider the phase transition in $CuGeO_3$ as belonging to the wide and well-known class of translation-rotation (TR) coupling of locally disordered variables. Examples of such kinds of phase transitions are well documented for systems where the local variable is an orientational moment such as in the ferroelastic phase transition in KCN (Ref. 14) and in the incommensurate and ferroelectric phase transitions in $NaNO_2$ and thiourea.[15,16] In the quasi-one-dimensional organic conductor of type (tetramethyltetraselenafulvalene)$2X$,[17] *where X* is either a ClO_4 (noncentrosymmetric) or a PF_6 (centrosymmetric) molecular ion, the electronic degree of freedom is the relevant variable. The alkali cyanides exhibit a phase transition with the ordering of rotationally disordered CN-elastic dipoles and with important changes in the lattice parameters and in the shear and longitudinal elastic constants. Finally, and more recently, the same kind of translation-rotation ordering formalism has been successfully applied to account for the phase transition in C_{60}.[18] In C_{60}, the complex rotational ordering of the fullerenes in the lattice results from the minimization of the intermolecular Coulomb interactions between point charges

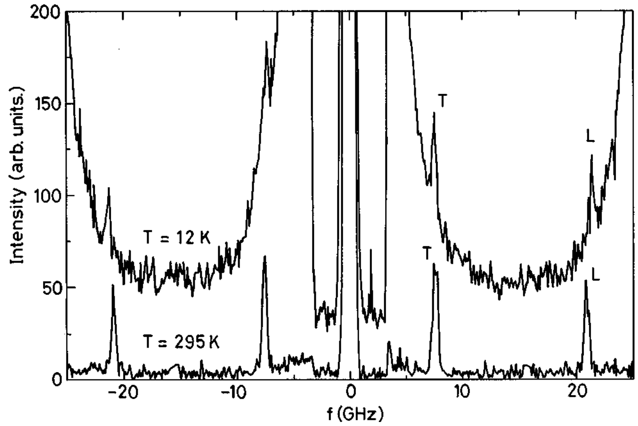

FIG. 1. Brillouin scattering spectra of $CuGeO_3$ at the temperatures $T=12$ K and $T=295$ K for the wave vector **q** parallel to the crystallographic c axis. The indices T and L above the Brillouin peaks indicate the transverse and longitudinal acoustic phonons.

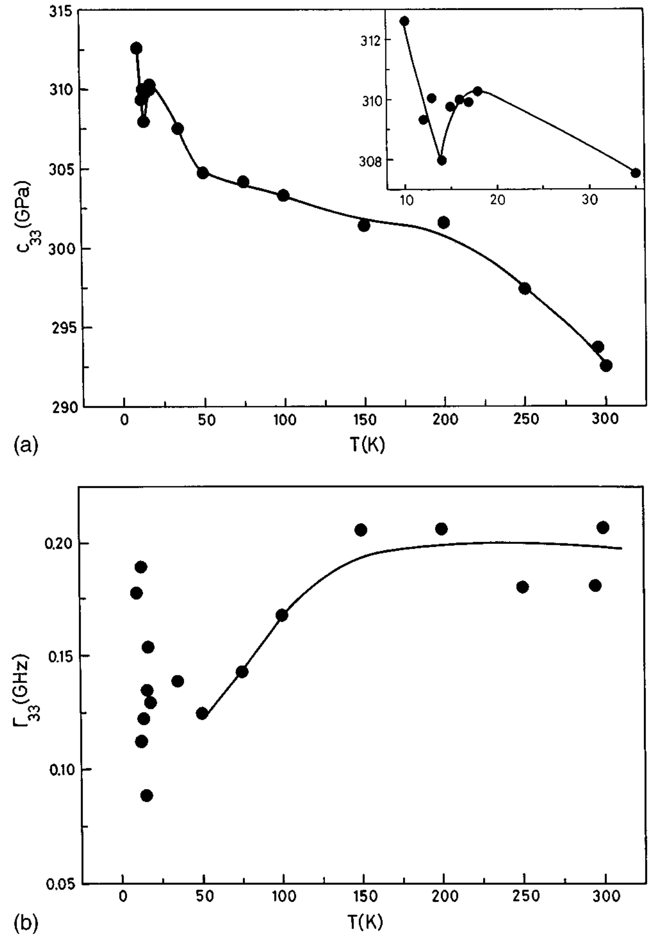

FIG. 2. (a) Temperature behavior of the longitudinal elastic constant c_{33}. The inset shows the immediate region about the spin-Peierls transition temperature ($T_{SP}\approx 14$ K). (b) Temperature behavior of the corresponding hypersonic attenuation Γ_{33}. In both cases the lines are only guides to the eye.

located at the single and double bonds. In this compound, as well as in $CuGeO_3$, the unit cell of the low-temperature structure is larger than the unit cell of the high-temperature structure, and hence the linear coupling between strain and order parameter is forbidden, being the relevant coupling quadratic in the order parameter and linear in strain.

For obvious reasons, our comprehension of the spin-Peierls phase transition in $CuGeO_3$ is not as developed as in the above-mentioned compounds. In what follows we will discuss the experimental results with regard to the physical implications of a TR mechanism at temperatures above T_{SP}. As we have remarked above, there is an alternative and more intuitive way of looking at the atomic distortion that consists of looking at the Cu-O(2)-Cu unit. Regardless of the O(1) contribution, the midpoint between the out-of-phase Cu displacements along the c axis and the O(2) displacements in the (**a**,**b**) plane is an inversion center of both the high- and low-temperature crystallographic structures. If we assign a ''+'' to one type of the combinations of atomic displacements, the ''−'' straightforwardly represents the complementary pattern of displacements. This observation leads to consider local pseudo-Ising occupational variables at these positions, and the structural ordering below T_{SP} is just the arrangement of these ''+'' and ''−'' pseudo-Ising variables, as has been experimentally observed. The TR coupling, as developed by Lamoen and Michel,[18] is a microscopic mechanism of interaction requiring a large knowledge of the atomic interaction potentials still lacking in $CuGeO_3$. Nevertheless, the great amount of work performed in these systems allows one to extract some general features for all these compounds. The expected anomalies in the elastic properties of the solid, above and below the phase transition, can be viewed along this line.

Ultrasonic (US) experiments have established the clear existence of a magnetoelastic coupling between the deformation and the spin-Peierls gap resulting in anomalies for the different elastic constants at the transition temperature.[19–22] To the authors's knowledge no ultrasonic data related to any of the shear constants of $CuGeO_3$ have been reported. The shear mode is a very sensitive probe for the existence of a TR coupling as a mechanism responsible for structural phase transitions. Therefore, the knowledge of its temperature behavior can serve to obtain information about additional mechanisms of a structural nature influencing the spin-Peierls transition.

From inelastic-neutron-scattering experiments,[23] one-dimensional quantum fluctuations in the paramagnetic state are expected to be present at temperatures well above T_{SP}, which in turn, through the TR coupling, may dynamically affect the elastic properties of the system. This is a point that has, unfortunately, been overlooked in previous experimental work, but we consider it to be most relevant for the understanding of the exact mechanism of the phase transition. In this paper we present the first set of measurements where besides the magnetoelastic coupling driving the spin-Peierls transition, the TR coupling is evidenced at temperatures above 50 K.

EXPERIMENT

We have used the 90A scattering geometry together with the angular-dependent Brillouin spectroscopy[24] (BS) in order to determine the relevant elastic constants in the (**b**,**c**) crystallographic plane of the $CuGeO_3$ sample. The light source was an Ar^+ laser with a wavelength of 514.5 nm and the

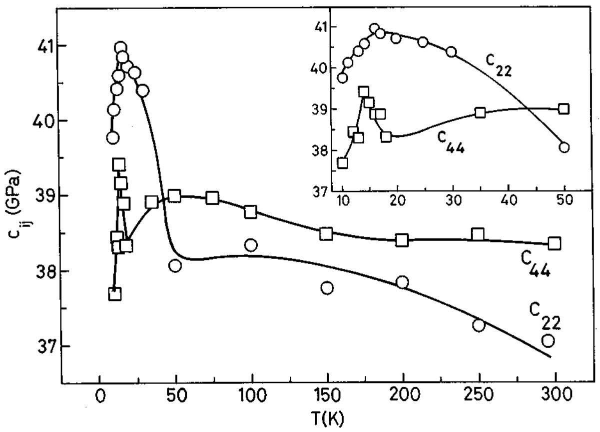

FIG. 3. Temperature behavior of the transverse elastic constant c_{44} (open squares) and of the longitudinal elastic constant c_{22} (open circles). Notice the crossing between both elastic constants at about 50 K. The inset shows the immediate region about the spin-Peierls transition temperature ($T_{SP} \approx 14$ K). The lines are only guides to the eye.

scattered light was analyzed using two Fabry-Perot interferometers mounted in tandem, working in an overall six-pass basis.[25]

The acoustic wave vector **q** can be selected to point along different directions in the plane giving information on the effective elastic constants (c_{eff}) in each direction: when the wave vector **q** coincides with a crystallographic axis of the orthorhombic symmetry, the effective elastic constant coincides with a well-defined elastic constant. In the case where **q** is parallel to **c** one obtains the longitudinal elastic constant c_{33} and two transverse (shear) elastic constants c_{44} and c_{55}.[26] In the case where **q** is parallel to **b**, one obtains the longitudinal elastic constant c_{22} and two transverse (shear) elastic constants c_{44} and c_{66}.[26] Usually c_{55} and c_{66} present a very low scattering cross section and c_{44} is the only shear mode to be observed. The 90A scattering geometry[24] has been shown not to depend on the refractive indexes of the sample and therefore the relationship between Brillouin shift (f), sound velocity (v), and effective elastic constant (c_{eff}) reads

$$v=\frac{f\lambda_0}{\sqrt{2}}; \quad c_{\mathrm{eff}}=\rho v^2,$$

where λ_0 is the laser wavelength in vacuum and ρ the temperature-dependent mass density.

The value of the density used to evaluate the elastic constants is $\rho=5100\ \mathrm{kg/m^3}$ and is considered constant in the whole temperature range, since the changes in density are one order of magnitude lower than the reported variations in the elastic constants as observed by US technique.

The temperature measurement and control was performed by means of a continuous-flow helium cryostate Optistat$^{\mathrm{CF}}$ (Oxford Instruments) and a temperature controller ITC-503 (Oxford Instruments).

Figure 1 shows two representative Brillouin spectra at the temperatures of 12 and 295 K. One observes simultaneously the peaks corresponding to the longitudinal and transverse acoustic phonons (in this case c_{33} and c_{44}, respectively).

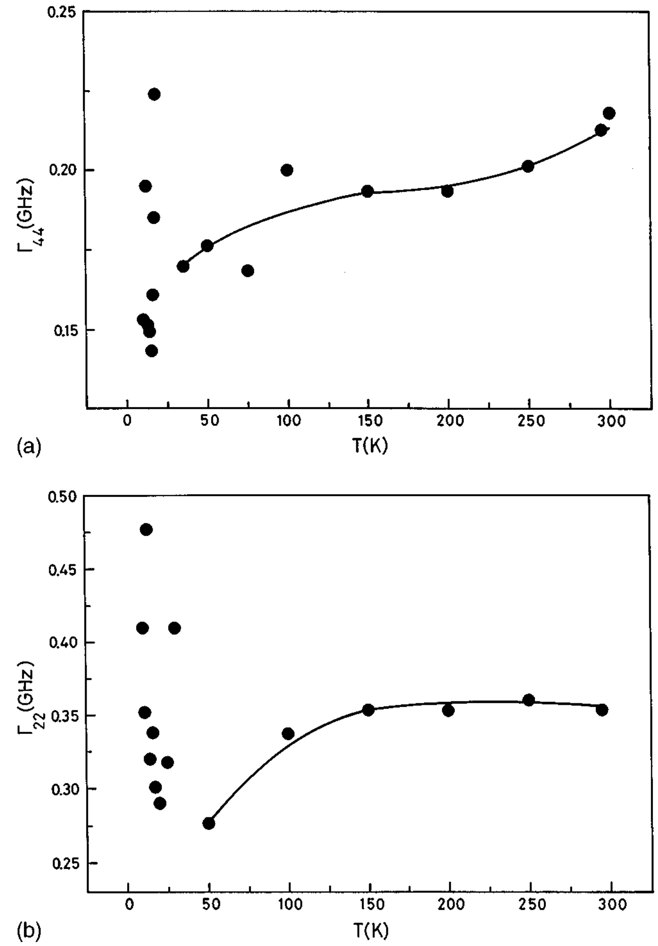

FIG. 4. Temperature behavior of the hypersonic attenuation Γ_{22} (a) and Γ_{44} (b). Γ_{22} corresponds to the elastic constant c_{22} and Γ_{44} to the elastic constant c_{44}. In both cases the lines are only guides to the eye.

RESULTS AND DISCUSSION

The temperature dependence ($10\ \mathrm{K}<T<\mathrm{RT}$) of the longitudinal elastic constants c_{22}, c_{33}, and of the shear elastic constant c_{44} and corresponding hypersonic attenuation (half width at half maximum, Γ_{ij}) are shown in Figs. 2, 3, and 4. The studied elastic constants show three clearly different temperature regimes: (i) from RT to 70 K, (ii) from 70 to 20 K, and (iii) around the spin-Peierls transition.

(i) In an orthorhombic system there are no restrictions concerning the relative values of the shear and longitudinal elastic constants, but it is extremely unusual for the longitudinal mode to lie below the transverse one. In fact, there are very few examples reporting values of shear modes being higher than those of the longitudinal modes.[27,28] Figure 3 evidences the small value of the elastic constant c_{22} being lower than the value of the shear elastic constant c_{44}. This uncommon fact agrees with the findings of a previous work[29] and with the existence of a longitudinal "soft mode" in the **b** direction as determined by neutron scattering.[10] The existence of a kind of layered crystallization [plane (**b**,**c**)] under certain growth conditions could be due to this elastic behavior.

Table I compares the elastic constants, at room temperature (RT), as determined by different experimental

TABLE I. Room-temperature values of different elastic constants as obtained by ultrasonic techniques (Ref. 21), Brillouin spectroscopy (Ref. 29), and this work.

c_{22} (GPa)	c_{33} (GPa)	c_{44} (GPa)
24.000 (Ref. 21)	300.000 (Ref. 21)	
41.835 (Ref. 29)	338.224 (Ref. 29)	40.833 (Ref. 29)
37.031	292.500	38.515

techniques.[29,21] A very striking fact is evidenced: while c_{33} (RT) is very similar for US technique (Ref. 21), and BS, that seems not to be the case for c_{22} (RT), for which BS and US data differ by a factor of about 2. In order to explain this discrepancy one could postulate the existence of an anisotropic acoustic dispersion between US technique (100 MHz) and BS ($\sim$8 GHz) that would correspond to the crossover from the fast-motion to the slow-motion regime of an entity to be defined. The observed difference in c_{22} (RT) could also be explained on the basis of the layered structure that poses some experimental difficulties in the propagation of the ultrasonic waves along the a and b axes of the crystal, due to the sample size required for ultrasonic measurements. Unfortunately, neither US attenuation data nor US elastic constants data have been reported in the whole temperature range explored in this study ($10\ \mathrm{K} < T < \mathrm{RT}$). Therefore, we are not in a position to rule out either of these two possibilities.

On lowering the temperature, a change in slope at about 150 K is observed in the temperature dependence of c_{33} and c_{44}. In contrast, c_{22} seems to follow a typical anharmonic behavior in this temperature range. This change has also been reported from US measurements[22] in the case of c_{33}. The hypersonic attenuation also shows a decrease around the same temperature. In order to derive any conclusion about the dynamic or static origin of this anomaly, it is essential to have a complete set of ultrasonic attenuation data as well as quasielastic-neutron-scattering data in the entire temperature range.

(ii) An overproportional increase of all the elastic constants is observed in the region of about 60 K, while the hypersonic attenuation remains unchanged [see Figs. 2(b) and 4]. This anomalous increase coincides with those reported for the thermal expansion coefficients[30] and the small hump observed in the magnetic susceptibility in the same temperature range.[3]

Notice that for the very first time we report the crossing, at a temperature of about 50–60 K, of c_{22} and c_{44} as a consequence of the different temperature gradients of these elastic constants (Fig. 3). Although there are no structural changes reported,[10] this crossing can be interpreted as a signature of local structural distortions that evolve with temperature, as probed by inelastic neutron scattering,[31] the O(2) oxygens in the (**a**,**b**) plane connecting the Cu^{2+} ions being responsible for this local disorder. These distortions are probably responsible for the very low values of c_{22} in the high-temperature regime and their influence on the other elastic constants becomes relevant below around 175 K as clearly seen in c_{33} and c_{44} plots. As the temperature is lowered the structural evolution proceeds to a point where the distortions freeze. At this temperature a dramatic increase in the values of c_{22} and c_{33} is observed while c_{44} shows a slight decrease. This behavior of c_{44} is very similar to the one observed in systems where the TR coupling plays the main role in the transition.[14,32] The magnetic susceptibility, i.e., the tendency for the system to locally remove the ground-state degeneracy is translated onto the lattice as an orientational disorder of the $GeO(2)_2$ units which, through the TR coupling, induces the observed anomalies in both the acoustic constants and in the thermal expansion coefficients. The measured crossing of c_{22} and c_{44} at around 60 K could be the result of the postulated structural evolution and distortion freezing prior the spin-Peierls transition.

(iii) The temperature evolution of the elastic constants, within this range, evidences the influence of the well-known spin-Peierls transition on the elastic behavior at about 14 K. However, as a result of the anisotropy of this magnetoelastic transition, there are differences in the shapes of the elastic constants curves when approaching the transition temperature from below. In the case of c_{33} the structural transition (*Pbmm* to *Bbcm* with a doubling of the a and c lattice parameters[33]) is characterized by a dip at about 14 K, in accordance with US measurements,[19–22] that could be interpreted in terms of a ''frustrated soft mode.'' This frustration lessens the displacive character of the phase transition as has been recently proposed.[33,34] Some qualitative discrepancies are found again between our data for the low-temperature behavior of c_{22} and those reported by US techniques.

In contrast to US technique we observe a cusp of c_{22} at T_{SP}. c_{44} clearly shows the spin-Peierls transition also as a cusp in clear contrast to c_{33}. This difference can be interpreted as the result of different magnetoelastic couplings between the Peierls gap and the corresponding deformation. The hypersonic attenuation shows, in all cases, an increase in the transition region. This increase correlates with the findings of pretransitional fluctuations of inelastic origin as seen by diffuse x-ray scattering,[35,3] which in turn is related to the appearance of the superlattice reflections below the spin-Peierls transition temperature and may also be related to the creation of dynamical dimers.

CONCLUSIONS

Summarizing, the BS measurements at room temperature confirm the existence of a very low energy longitudinal acoustic mode c_{22}, lower than the c_{44} transverse mode. There exist clear discrepancies with the temperature behavior of c_{22} reported by ultrasonic experiments. The origin of these discrepancies is still unclear. On the other hand, the anomalies observed in the elastic behavior at around 60 K correlate with the observed anomalies in the expansion coefficient and the magnetic susceptibility, and can be interpreted in terms of the existence of structural distortions in the system. In fact, the presence of some degree of disorder at high temperatures, either dynamic or static, may be responsible for the very low values of c_{22}.

The dramatic increase in the values of c_{22} and c_{33} and the crossing between c_{22} and c_{44} are hints for the existence of a TR coupling mechanism responsible for the elastic behavior prior to the magnetoelastic coupling at T_{SP}.

Within this frame, we propose that the TR coupling is related to the activated motion of the O(2) oxygens in the (**a**,**b**) plane connecting the Cu^{2+} ions, and affecting the CuO_6

octahedrons and GeO_4 tetrahedrons. In this way, the dynamics of the magnetic ions evolves to a point at which the magnetic interaction is triggered. This is consistent with the observed x-ray diffuse scattering at temperatures well above T_{SP}. This assertion does not rule out the existence of a magnetoelastic coupling that it is evidenced by the critical behavior of the elastic constant. In other words, TR coupling promotes a dimerization that is fully accomplished when the magnetic interaction becomes efficient, then the degeneracy of the magnetic ground state breaks down leading to the well-known spin-Peierls state. It seems also clear that the magnetism operating in the system on approaching T_{SP} induces additional distortions in the lattice via magnetoelastic coupling.

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[1] J. W. Bray, L. V. Interrante, I. S. Jacobs, and J. C. Bonner, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1982), Vol. 3, pp. 353–415.
[2] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[3] J. P. Pouget, L. P. Regnault, M. Ain, B. Hennion, J. P. Renard, P. Veillet, G. Dhalenne, and A. Revcolevschi, Phys. Rev. Lett. **72**, 4037 (1994).
[4] M. Arai, M. Fujita, M. Motokawa, J. Akimitsu, and S. M. Bennington, Phys. Rev. Lett. **77**, 3649 (1996).
[5] J. E. Lorenzo, L. P. Regnault, B. Hennion, M. Aïn, F. Bourdarot, J. Kulda, G. Dhalenne, and A. Revcolevschi, J. Phys.: Condens. Matter **9**, L211 (1997).
[6] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. **65**, 1182 (1996).
[7] G. Castilla, S. Chakravarty, and V. J. Emery, Phys. Rev. Lett. **75**, 1823 (1995).
[8] J. Riera and A. Dobry, Phys. Rev. B **51**, 16 098 (1995).
[9] I. Yamada, M. Nishi, and J. Akimitsu, J. Phys.: Condens. Matter **8**, 2625 (1996).
[10] J. E. Lorenzo, K. Hirota, G. Shirane, J. M. Tranquada, M. Hase, K. Uchinokura, H. Kojima, I. Tanaka, and Y. Shibuya, Phys. Rev. B **50**, 1278 (1994).
[11] G. Grüner, *Density Waves in Solids* (Addison-Wesley, Reading, MA, 1994).
[12] M. Braden, B. Hennion, W. Reichardt, G. Dhalenne, and A. Revcolevschi (unpublished).
[13] M. Braden, G. Wilkendorf, J. Lorenzana, M. Aïn, G. J. McIntyre, M. Behruzi, G. Heger, G. Dahlenne, and A. Revcolevschi, Phys. Rev. B **54**, 1105 (1996).
[14] U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).
[15] D. Durand, F. Dénoyer, R. Currat, and M. Lambert, in *Incommensurate Phases in Dielectrics*, edited by A. P. Levanyuk (Elsevier, Amsterdam, 1986).
[16] F. Dénoyer and R. Currat, in *Incommensurate Phases in Dielectrics*, Ref. 15.
[17] R. Moret, J. P. Pouget, R. Còmes, and K. Bechgaard, Phys. Rev. Lett. **49**, 1008 (1982).
[18] D. Lamoen and K. H. Michel, Phys. Rev. B **48**, 807 (1993).
[19] M. Saint-Paul, P. Monceau, and A. Revcolevschi, Solid State Commun. **93**, 7 (1995).
[20] M. Poirier, M. Castonguay, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **51**, 6147 (1995).
[21] M. Saint-Paul, G. Reményi, N. Hegmann, P. Monceau, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **52**, 15 298 (1995).
[22] M. Poirier, M. Castonguay, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **52**, 16 058 (1995).
[23] J. E. Lorenzo and L. P. Regnault (unpublished).
[24] J. K. Krüger, in *Optical Techniques to Characterize Polymer Systems*, edited by H. Bässler (Elsevier, Amsterdam, 1989).
[25] J. R. Sandercock, in *Trends in Brillouin Scattering. Studies of Opaque Materials, Supported Films, and Central Modes*, edited by M. Cardona and G. Güntherodt, Topics in Applied Physics, Vol. 51 (Springer, Berlin, 1982), p. 173.
[26] B. A. Auld, *Acoustic Fields and Waves in Solids* (Wiley, New York, 1973).
[27] S. Haussühl, Z. Kristallogr. **118**, 33 (1963).
[28] A. G. Kalinichev, J. D. Bass, B. N. Sun, and D. A. Payne, J. Mater. Res. **12**, 2623 (1997).
[29] H. Yamaguchi, M. Yamaguchi, and T. Yagi, J. Phys. Soc. Jpn. **64**, 1055 (1995).
[30] H. Winkelmann, E. Gamper, B. Büchner, M. Braden, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **51**, 12 884 (1995).
[31] M. Arai, M. Fujita, K. Ubukata, T. Bokui, K. Tabata, H. Ohta, M. Motokawa, T. Otomo, K. Ohiyama, M. Mino, J. Akimitsu, and O. Fujita, J. Phys. Soc. Jpn. **63**, 1661 (1994).
[32] J. K. Krüger, R. Jiménez, K.-B. Bohn, J. Petersson, J. Albers, A. Klöpperpieper, E. Sauerland, and H. E. Müser, Phys. Rev. B **42**, 8537 (1990).
[33] K. Hirota, G. Shirane, Q. J. Harris, Q. Feng, R. J. Birgeneau, M. Hase, and K. Uchinokura, Phys. Rev. B **52**, 15 412 (1995).
[34] L. P. Regnault, M. Ain, B. Hennion, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **53**, 5579 (1996).
[35] J. P. Schoffel, J. P. Pouget, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **53**, 14 971 (1996).