Magnetoelastic coupling in $CuFeO_2$

G. Quirion[1], M.J. Tagore[1], M.L. Plumer[1] and O.A. Petrenko[2]

[1] Department of Physics and Physical Oceanography, Memorial University, St. John's, Newfoundland, Canada, A1B 3X7

[2] Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom

E-mail: gquirion@mun.ca

Abstract. Ultrasonic velocity data obtained on $CuFeO_2$ are re-analyzed in the context of a Landau free energy which includes spin-lattice coupling. This comprehensive model simultaneously accounts for the elastic and magnetic properties of $CuFeO_2$ at zero field. Softening of the elastic constants C_{11}, C_{44}, and especially C_{66}, ineluctably indicates that the $R\overline{3}m \rightarrow C2/m$ structural transition at $T_{N1} = 13.7$ K is primarily *pseudoproper ferroelastic*. The present analysis also suggests that the elastic anomalies observed at T_{N2} are dominated by magnetoelastic coupling and strengthens the conclusion that the unusual properties of $CuFeO_2$ are a consequence of the interplay between its magnetism and elastic deformations.

1. Introduction

The properties of the multiferroic compound $CuFeO_2$ have been the object of many theoretical and experimental investigations in recent years. This rhombohedral-lattice frustrated antiferromagnetic system is well known for its unusual magnetic phase diagram and its unconventional field-induced magnetoelectric effect correlated with the stabilization of a non-collinear spin configuration [1]. In zero magnetic field, successive magnetic phase transitions occur from paramagnetic to an incommensurate collinear spin polarization at $T_{N1} = 13.7$ K, followed by a period-4 collinear ($\uparrow\uparrow\downarrow\downarrow$) spin modulation at $T_{N2} \simeq 10.5$ K, both with $\mathbf{S}||\hat{\mathbf{c}}$. As the magnetic anisotropy of the Fe^{3+} ions is expected to be small, it has been recently proposed that the spin-lattice coupling in $CuFeO_2$ is more likely responsible for the stability of collinear magnetic structures [2, 3]. Considering the affluence of experimental [4, 5, 6] and numerical [3] evidences indicating that magnetoelastic effect must play a vital role in the properties of $CuFeO_2$, the focus of this work is to explore this effect within the frame work of a Laudau free energy. The approach adopted here is to compare the model predictions to the elastic properties of $CuFeO_2$ obtained from recent ultrasonic velocity measurements [7].

2. *Pseudoproper ferroelastic* model

In a previous paper [7], we presented a soft-mode Landau free energy that accounts for most of the temperature dependence of the elastic properties of $CuFeO_2$ at zero magnetic field. Our velocity measurements, shown in Fig. 1, confirm that the elastic properties are strongly coupled to the magnetic order taking place at low temperatures. The most striking feature shown in Fig. 1 is the large variation in the value of the velocity as the temperature approaches $T_{N1} = 13.7$ K. This variation, produced by the softening of the lattice structure, is especially pronounced for transverse waves traveling along x and polarized along y, $V_{Tx}P(y)$. A similar temperature dependence is also noted for longitudinal waves propagating along x (V_{L_x}) and shear modes associated with $V_{Tz}P(x)$. According to our analysis [7], this peculiar temperature dependence can be attributed to a *pseudoproper ferroelastic* phase transition [8] which coincides with the magnetic phase transition at T_{N1}. In conformity with the $R\bar{3}m$ high temperature crystal symmetry, a two dimensional order parameter (η_1, η_2) can be associated with the softening of E-symmetric modes belonging to the D_{3d} group [8, 9]. Results derived in [7] are reproduced in Table 1. For simplification the coupling terms $[\beta_1(e_1 + e_2) + \beta_3 e_3](\eta_1^2 + \eta_2^2)$ have been neglected, along with the elastic constant $C_{13} = 0$. As shown in Fig. 1, numerical predictions based on these results agree particularly well with most experimental data obtained above T_{N2}. It is clear that the nature of the $R\bar{3}m \rightarrow C2/m$ structural phase transition is driven by the softening of the E-symmetric mode. Nevertheless, this model fails to reproduce observations at lower temperatures. In particular, it gives no explanation for the temperature dependence of C_{33}, which, as previously proposed [7] could be attributed to magnetoelastic effects.

3. Magnetoelastic coupling

It has recently been shown, using a nonlocal free energy functional to represent the spin-spin interaction, an effective free energy for the spin contribution at $H = 0$ can be written as [10]

$$F_S = A_Q S^2 - J_z S^2 + B_{IC} S^4 - B_u S^4 \Delta_{4\mathbf{Q},\mathbf{G}} \ . \tag{1}$$

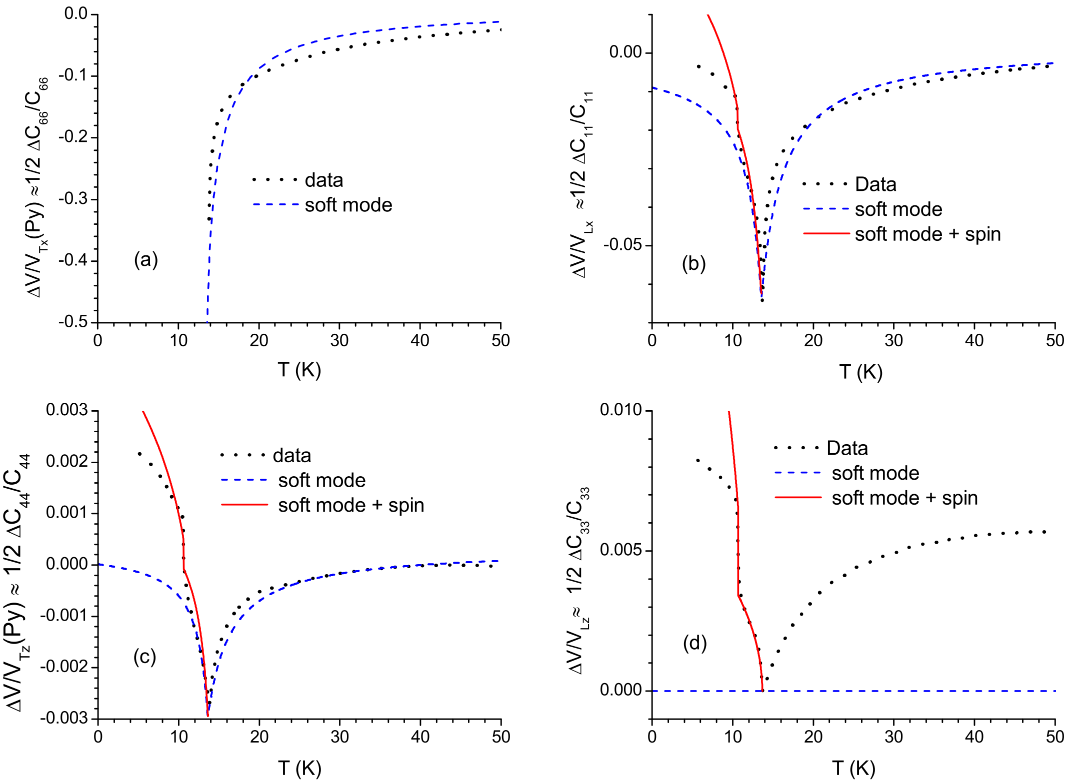

Figure 1. Temperature dependence of the relative velocity variation of longitudinal (L) and transverse (T) modes.

Table 1. Temperature dependence of the velocity of selected acoustic modes for a $R\bar{3}m \to C2/m$ pseudo-ferroelastic phase transition with $\eta_1 = \sqrt{\frac{a(T_{N1}-T)}{2B}}$, $A(T) = a(T - T_o)$.

modes	Trigonal $R\bar{3}m$	Monoclinic C2/m	
	soft-mode	soft-mode	Spin
$\frac{\Delta V}{V_{Lx}} \simeq \frac{1}{2}\frac{\Delta C_{11}}{C_{11}}$	$-\frac{\delta_1^2}{2C_{11}A(T)}$	$-\frac{1}{2C_{11}}\frac{\delta_1^2}{A(T_{N1})+2B\eta_1^2}$	$-\frac{\beta_1^2}{4C_{11}B_{IC}} + \frac{2\gamma_1}{C_{11}}S_z^2$
$\frac{\Delta V}{V_{Lz}} \simeq \frac{1}{2}\frac{\Delta C_{33}}{C_{33}}$	0	0	$-\frac{\beta_3^2}{4C_{11}B_{IC}} + \frac{\gamma_3}{C_{33}}S_z^2$
$\frac{\Delta V}{V_{Tz}(Px)} \simeq \frac{1}{2}\frac{\Delta C_{44}}{C_{44}}$	$-\frac{\delta_2^2}{2C_{44}A(T)}$	$-\frac{1}{2C_{44}}\frac{\delta_2^2}{A(T_{N1})+2B\eta_1^2}$	$+\frac{\gamma_4}{C_{44}}S_z^2$
$\frac{\Delta V}{V_{Ty}(Px)} \simeq \frac{1}{2}\frac{\Delta C_{66}}{C_{66}}$	$-\frac{\delta_1^2}{2C_{66}A(T)}$	$-\frac{1}{2C_{66}}\frac{\delta_1^2}{A(T_{N1})}$	$+\frac{\gamma_1-\gamma_2}{C_{66}}S_z^2$

with $S = S_z$, $A_Q = a_sT + J_Q$, and $B_{IC} > 0$. Since the effective exchange coupling parameter J_Q must minimize the spin-spin interaction, values for the incommensurate and commensurate spin modulations are identified as J_{IC} and J_C. An anisotropy term, with $J_z > 0$, is also necessary in order to account for collinear spin configurations with $\mathbf{S}||\hat{z}$. The Kronecker delta function $\Delta_{4\mathbf{Q},\mathbf{G}}$ indicates that Umklapp terms are allowed whenever the spin wave vector modulation $4\mathbf{Q}$ coincides with one of the reciprocal lattice vector $\mathbf{G}$. This term is particularly important as it contributes to the stability of the period-4 phase. Minimizing the free energy (1) with respect to S, we obtain

$$\begin{array}{llll} T_{N2} < T < T_{N1}, & S_{IC}^2 = \frac{a_s(T_{N1}-T)}{2B_{IC}}, & F_{IC} = -\frac{a_s^2(T-T_{N1})^2}{4B_{IC}}, & \text{with} \quad T_{N1} = (-J_{Q_{IC}} + J_z)/a_s \\ T < T_{N2}, & S_C^2 = \frac{a_s(T_s-T)}{2(B_{IC}-B_u)}, & F_C = -\frac{a_s^2(T-T_s)^2}{4(B_{IC}-B_u)}, & \text{with} \quad T_s = (-J_{Q_C} + J_z)/a_s. \end{array} \tag{2}$$

The condition $F_C = F_{IC}$ at $T = T_{N2}$, gives the relation

$$\frac{B_{IC}}{B_{IC} - B_u} = \left(\frac{T_{N2} - T_{N1}}{T_{N2} - T_s}\right)^2. \tag{3}$$

Setting parameters $a_s = 1, J_z = 0.1, B_{IC} = 0.5, T_s = 11.5\ K, T_{N2} = 10.3\ K, T_{N1} = 13.7\ K$, and $B_u = 0.46$, Eq.(2) leads to the usual mean field continuous transition at T_{N1} followed by a first order phase transition at T_{N2}, in accord with the experimental observations.

A total free energy, which involves the spin (Eq. 1) and soft-mode degrees of freedom, can be expanded as

$$F_t(S, e_\alpha, \eta) = F_\eta + F_{\eta e} + F_e + F_S + F_{Se} + F_{\eta S} \tag{4}$$

in order to include the magnetoelastic coupling. Explicit expressions for the first three terms, associated with the *pseudoproper ferroelastic* free energy, can be found in [7]. All magnetoelastic coupling terms must be invariant under time reversal and $R\bar{3}m$ symmetry operations. Coupling between S_z and strain components e_α (Voigt notation) takes the form

$$\begin{aligned} F_{Se} &= \beta_1 S_z^2(e_1 + e_2) + \beta_3 S_z^2 e_3 + \gamma_1(2e_1^2 + 2e_2^2 + e_6^2)S_z^2 + \gamma_2(4e_1e_2 - e_6^2)S_z^2 \\ &+ \gamma_3 e_3^2 S_z^2 + \gamma_4(e_4^2 + e_5^2)S_z^2 + \gamma_5((e_1 - e_2)e_4 + e_5e_6)S_z^2\ , \end{aligned} \tag{5}$$

where linear $(e_\alpha S_z)$ and quadratic $(e_\alpha^2 S_z^2)$ terms are included. As outlined in [7], coupling between the soft-mode and S_z gives only one term, $F_{\eta S} = \gamma(\eta_1^2 + \eta_2^2)S_z^2$. Minimization of the full free energy (4) gives $S_z^2 \propto (\eta_1^2 + \eta_2^2)$ and

$$\begin{aligned}
e_1 - e_2 &= -\tfrac{2\ (\delta_1\ C_{44} - \delta_2\ C_{14})}{C_{44}(C_{11}-C_{12}) - 2C_{14}^2}\ \eta_1, & e_4 &= \tfrac{\delta_2\ (C_{11}-C_{12}) - 2\delta_1\ C_{14}}{C_{44}(C_{11}-C_{12}) - 2C_{14}^2}\ \eta_1, \\
e_1 + e_2 &= -\tfrac{2\ \delta_3}{C_{11}-C_{12}}\ (\eta_1^2 + \eta_2^2) - \tfrac{2\ \beta_1}{C_{11}-C_{12}}\ S_z^2, & e_5 &= \tfrac{(\delta_1\ C_{14} - \delta_2\ C_{66})}{C_{44}C_{66} - C_{14}^2}\ \eta_2, \\
e_3 &= -\tfrac{\delta_4}{C_{33}}\ (\eta_1^2 + \eta_2^2) - \tfrac{\beta_3}{C_{33}}\ S_z^2, & e_6 &= \tfrac{(\delta_2\ C_{14} - \delta_1\ C_{44})}{C_{44}C_{66} - C_{14}^2}\ \eta_2.
\end{aligned} \tag{6}$$

The magnetoelastic effects on the sound velocity is presented in the last column of Table 1. According these results, the linear coupling constants, β_1 and β_3, should give rise to a step like variation at T_{N1} on V_{Lx} and V_{Lz}. Since no such variation is observed, these terms are neglected. The model prediction for $\Delta V/V_{Lz}$ is then particularly interesting as it indicates that longitudinal modes propagating along z can be used to probe the temperature dependence the magnetic order parameter S_z. In order to test this prediction, the temperature dependence of $\Delta V/V_{Lz}$ has been compared to Eq. 2, with S_{IC}^2 replaced by $a_s(T_{N1} - T)^{2\beta}$. As shown in Fig. 1d, a very good agreement is obtained when the mean field critical exponent is replaced with the fitted value $\beta = 0.25$. We note that this value is significantly lower than of the XY universality class [10]. This result has been used to calculate the magnetoelastic effect on the velocity of other modes. Finally, Fig. 1 also shows numerical predictions which consider both ferroelastic and magnetoelastic effects. For C_{11}, C_{44}, and especially C_{33}, there is much improved agreement between the model's predictions and the experimental data when spin-lattice coupling is accounted for.

4. Conclusions

This study presents an analysis of magnetoelastic effects on the ultrasonic velocity data previously obtained for $CuFeO_2$ [7]. In order to fully account for the experimental observations, two types of order parameters are required. While, close to T_{N1}, anomalies observed on velocity measurements are driven by E-symmetric soft-modes, our numerical analysis indicates that magnetoelastic effects are responsible for variations observed at T_{N2}. The interplay between these two mechanisms is particularly evident on C_{33} where the temperature dependence at low temperatures is well reproduced by a magnetoelastic coupling term, with no contribution from the soft-mode. Within the Landau model considered in this work, Eq. 6 also indicates that the $R\bar{3}m \rightarrow C2/m$ symmetry change observed at T_{N1} is associated with the order parameter $\eta = (\eta_1, 0)$ with the spin modulation S_z serving in a second role.

Acknowledgments

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References

[1] Kimura T, Lashley J C and Ramirez A P 2006 *Phys. Rev. B* **73** 220401(R)
[2] Plumer M L 2007 *Phys. Rev. B* **76** 144411
[3] Wang F and Vishwanath A 2008 *Phys. Rev. Lett.* **100** 077201
[4] Ye F, Ren Y, Huang Q, Fernandez-Baca J A, Dai P, Lynn J W and Kimura T 2006 *Phys. Rev. B* **73** 220404(R)
[5] Terada N, Narumi Y, Sawai Y, Katsumata K, Staub U, Tanaka Y, Kikkawa A, Fikui T, Kindo K, Yamamoto T, Kanmuri R, Hagiwara M, Toyokawa H, Ishikawa T and Kitamura H 2007 *Phys. Rev. B* **75** 224411
[6] Terada N, Mitsuda S, Tanaka Y, Tabata Y, Katsumata K and Kikkawa A 2008 *J. Physical Society of Japan* **77** 054701
[7] Quirion G, Tagore M J, Plumer M L and Petrenko O A 2008 *Phys. Rev. B* **77** 094111
[8] Tolédano P, Fejer M M and Auld B A 1983 *Phys. Rev. B* **27** 5717 – 5745
[9] Tinkhan M 2003 *Group Theory and Quantum Mechanics* (Dover Publications, INC)
[10] Plumer M L 2008 *Phys. Rev. B* **78** 094402