ARTICLES

ESR study of the incommensurate phase in doped $(NH_4)_2ZnCl_4$

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The ESR line shapes of $(NH_4)_2ZnCl_4$ crystals doped with Mn^{2+} were studied in a range of temperatures from 160 to 80 °C. It was found that the crystal undergoes an incommensurate phase transition at 135 °C and an incommensurate-commensurate transition at 92 °C. The form and temperature dependence of the ESR spectra throughout these changes are in good agreement with the predictions of the phase-soliton theory. The parameters h_1 and h_2 determining the variation of the resonant magnetic field show a power-law behavior as a function of temperature. The critical exponent β of this crystal was determined two independent ways to be 0.36 ± 0.03. The soliton density does not change significantly during the whole incommensurate phase and drops abruptly to zero at the incommensurate-commensurate transition, a behavior that is quite different from those of other incommensurate systems. [S0163-1829(98)01614-2]

INTRODUCTION

The ferroelectric compound ammonium tetrachlorozincate, $(NH_4)_2ZnCl_4$, undergoes a transition from an orthorhombic structure with space group $D_{2\nu}^{16}$ $(Pnam)$ and unit-cell volume $a_0b_0c_0$ (Ref. 1) to an incommensurate phase at about 133 °C and a second transition from the incommensurate phase to the commensurate structure with space group $C_{2\nu}^{9}$ $(Pn21a)$ and lattice constants $a=4a_0$, $b=b_0$, $c=c_0$ (Ref. 1) at 92 °C.[2] The incommensurate phase is characterized by the fact that the fundamental crystal structure is modulated with a wavelength λ which is not commensurate with the underlying crystal lattice constant a, i.e., the ratio λ/a cannot be expressed as a ratio of two integers so that the translation symmetry is lost. In this phase, there is essentially an infinite number of physically inequivalent sites for the Zn ion to occupy. When Mn^{2+} is substituted randomly for Zn^{2+}, each Mn^{2+} experiences a slightly different environment which is reflected in the electron-spin-resonance spectrum. The observed ESR signal is therefore a superposition of many individual lines. This is in contrast to the high-temperature case where the environment of each ion is identical, and the low-temperature commensurate phase where there are four inequivalent sites. In this paper we present a quantitative analysis of the ESR spectra which is in excellent agreement with the predictions of the one-dimensional phase soliton model.

THEORY

The spin Hamiltonian for the spin $S=5/2$, Mn^{2+} ion is

$$\mathcal{H}=\mu_B\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}+\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{T}\cdot\mathbf{I}, \tag{1}$$

where the nuclear spin $I=5/2$. The g factor $\mathbf{g}$ and the hyperfine coupling constant $\mathbf{T}$ are nearly isotropic, and the fine structure coupling $\mathbf{D}$ is sensitive to the lattice deformation. The principle values of the $\mathbf{g}$ and $\mathbf{T}$ tensors are $g=2.004$ and $T=97$ G.[3]

Therefore Eq. (1) can be rewritten as

$$\mathcal{H}=g\mu_BS\cdot B+D\left[S_z^2-\frac{1}{3}S(S+1)\right]+E(S_x^2-S_y^2)+TS\cdot I. \tag{2}$$

The resonant field B_r is then given, to first order in the crystal-field splitting, by

$$B_r=B_0+M_IT+\frac{3}{2}(2M_s-1)d, \tag{3}$$

where $d=d_a\sin^2\theta\cos^2\varphi+d_b\sin^2\theta\sin^2\varphi+d_c\cos^2\theta$ and θ, φ are the spherical coordinates of the direction of the applied magnetic field in the $\mathbf{D}$ principle coordinate system, and d_a, d_b, d_c are the principle values of $\mathbf{D}$.

The complete ESR spectrum consists of five groups of six lines each. To maximize the sensitivity to variations in $\mathbf{D}$ we analyze the shape of the line corresponding to $M_I=5/2$, $M_S=5/2$ in Eq. (3).

The modulation wave in the incommensurate phase is given by[4]

$$u=u_0\cos\phi(x), \tag{4}$$

where u_0 is the amplitude of the distortion, or the order parameter, and $\phi(x)$ is a solution of the sine-Gordon equation[5]

$$\frac{d^2\phi}{dx^2}=-\alpha^2\sin(p\phi). \tag{5}$$

The parameter α^{-1} measures the width of the soliton, and p is the order of commensurability with $p=4$ in the present case.[2] The resonant field Eq. (3) can be expressed as a power expansion in the modulation amplitude u:

$$B_r = B_0 + h_1 \cos\phi(x) + \frac{1}{2} h_2 \cos^2\phi(x) + \cdots . \quad (6)$$

In the incommensurate phase, $\cos\phi(x)$ varies nearly continuously from -1 to $+1$, while in the commensurate phase, it takes on discrete values.

The probability of finding a resonant signal at a magnetic field $B{:}f(B_r)dB_r$, should be proportional to the probability of finding an atom (or ion) with a particular displacement u, which is given by $P(u)du = P(x)dx$. Since $P(x)$ is uniform, the probability distribution of resonant fields can be given by

$$f(B_r) = \frac{\text{const}}{\left|\frac{dB_r}{dx}\right|} = \frac{\text{const}}{|(d\phi/dx)(h_1 + h_2\cos\phi)\sin\phi|}, \quad (7)$$

where $d\phi/dx$ is obtained from the first integral of the sine-Gordon equation (5):

$$\frac{d\phi}{dx} = 2\frac{\alpha}{\sqrt{p}}\left[\delta^2 + \cos^2\left(\frac{1}{2}p\phi\right)\right]^{1/2}, \quad (8)$$

where $\delta^2 = (c - p\alpha^2)/2p\alpha^2$ and c is an integration constant, $c \geqslant p\alpha^2$.

The parameter δ is closely related to the soliton density n_s, which is generally defined as the ratio of the soliton width to the intersoliton spacing, and which vanishes in the commensurate limit and approaches one in the plane-wave limit $\phi(x) = kx$. The relation between the two quantities is[4]

$$n_s = \frac{\pi}{2K(\delta)}, \quad (9)$$

where $K(\delta)$ is the elliptic integral of the first kind defined by

$$K(\delta) = \int_0^{\pi/2}\left[1 - \left(\frac{1}{1+\delta^2}\right)\sin^2\theta\right]^{-1/2} d\theta. \quad (10)$$

The line intensity profiles can be calculated by convoluting the distribution of resonant field $f(B_r)$ with a Lorentzian line shape of width σ:

$$I(B) = \int_0^\infty f(B_r)L(B - B_r, \sigma)dBr. \quad (11)$$

The predicted line shape $I(B)$ depends on the parameters σ, h_1, h_2, and δ. By fitting the measured spectra to the line shape (11), we can determine h_1, h_2, and δ and compare them with the predictions of the phase-soliton model.

RESULTS AND DISCUSSIONS

Single crystals of $(NH_4)_2ZnCl_4$ doped with about 0.1% of Mn^{2+} were grown by slow evaporation of an aqueous solution at room temperature. The Mn^{2+} substitutes randomly for Zn^{2+} and is surrounded by four Cl^- ions. The crystals are colorless and transparent.

In the high-temperature (normal) phase ($T > 134.8$ °C), characteristic ESR lines of Mn^{2+} were observed at a microwave frequency 9.1 GHz (Fig. 1). The fine and hyperfine structures of the spectrum are in very good agreement with the Hamiltonian (1). The spectrum also shows a strong angular dependence due to the position of the Mn^{2+} relative to the four Cl^- ions. In Fig. 1, the magnetic field is perpendicular to the a axis of the crystal and the sample was rotated around the a axis to a position so that the spectrum is well resolved. On cooling below 134.8 °C, the resonant lines become broader and eventually split into doublets. A least-squares (LSQ) fit of the experimental spectra to the theoretical line shape (11) was performed to extract the parameters h_1, h_2, and δ (Fig. 2). We noticed that the linewidth decreases slightly and the center of the line B_0 increases as the temperature goes down, and these parameters were included in the LSQ fitting. The temperature dependence of h_1, h_2, and n_s shown in Figs. 3 and 4 clearly demonstrates that the crystal undergoes two transitions, one at 134.8 °C from normal to an incommensurate phase and an incommensurate to commensurate ''lock-in'' phase transition at 92 °C. The line shape was found to be very sensitive to the values of h_1 and h_2, but not very sensitive to the value of δ. A 50% change in δ only gives about a 10% change in the simulated spectra when the value of δ is in the range of 10^{-4}–10^{-3}. However, because n_s is slowly varying with δ for small δ [Eq. (9) and Fig. 5], this insensitivity does not prevent us from getting a reasonably good estimation for n_s. A constant initial phase ϕ_0 can be added to ϕ in Eqs. (5) and (6), to which the line shape is very sensitive in the low-temperature incommensurate range. Its value was found to be zero for the best fitting.

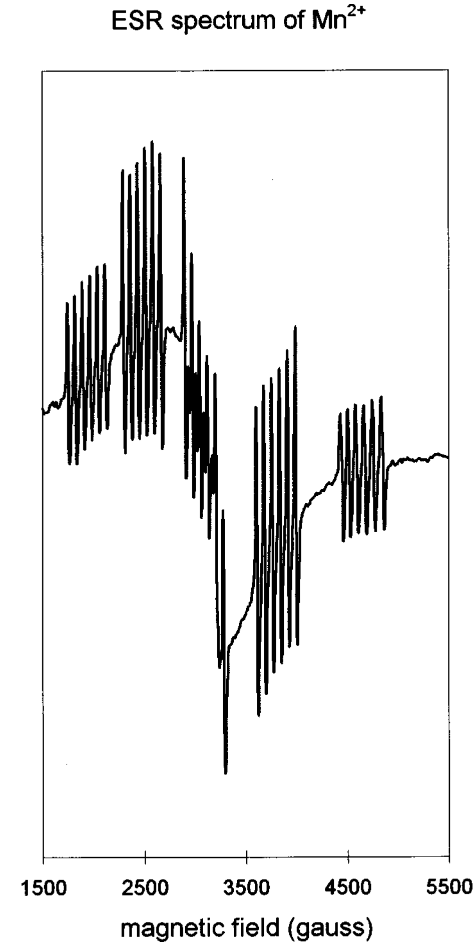

FIG. 1. Complete ESR spectrum of Mn^{2+}, normal phase, with a axis perpendicular to the applied magnetic field.

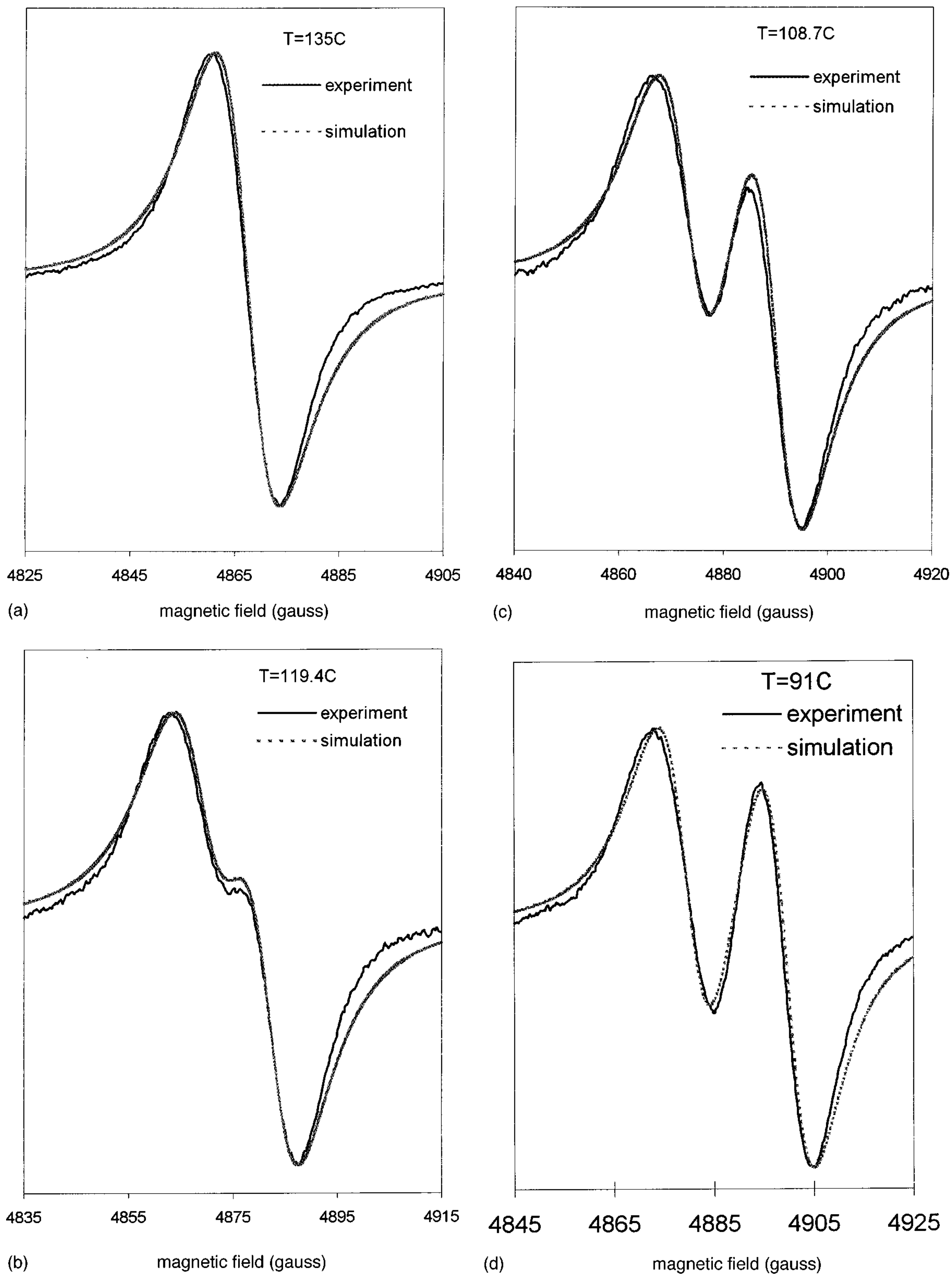

FIG. 2. Experimental spectra plus four examples of line-shape simulation. The derivative of the observed ESR line intensity of the highest field [$M_I=-5/2$, $M_S=5/2$, Eq.(3)] hyperfine line in the spectrum of Mn^{2+} is shown plotted as a function of external magnetic field.

In the critical region near T_I the order parameter u_0 is expected to vary with temperature as $u_0 \sim (T_I-T)^\beta$, which should be reflected in the temperature dependence of h_1 and h_2. Values of β for other incommensurate crystals have been reported: for Rb_2ZnCl_4 $\beta=0.35\pm0.03$[4,6–9] for Rb_2ZnBr_4 $\beta=0.35\pm0.03$,[10] for KH_2PO_4 $\beta=0.33\pm0.02$,[11] for $ThBr_4$ $\beta=0.34\pm0.02$.[12]

In Fig. 6 we show $\ln(h_1)$ and $\ln(h_2)$ plotted versus $\ln(T_I-T)$, where T_I is the incommensurate phase-transition temperature. The linear relationship between them indicates the expected power-law behavior of h_1 and h_2:

$$h_1=c_1(T_I-T)^\beta, \tag{12}$$

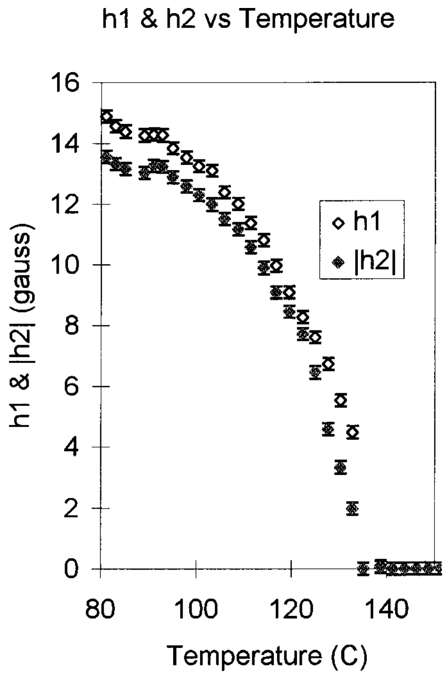

FIG. 3. Temperature dependence of parameters h_1 and h_2 showing incommensurate phase transition at about 134.8 °C. Values of h_2 are negative so absolute values are plotted in the graph.

$$h_2 = c_2 (T_I - T)^{2\beta}. \tag{13}$$

The critical exponents β and 2β are determined independently form the slopes of the straight lines to be 0.35±0.03 and 0.74±0.04. The uncertainty in the critical exponents is

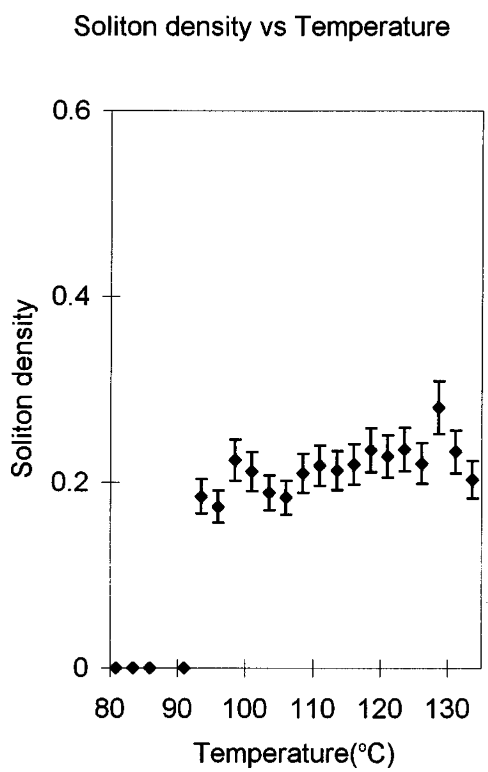

FIG. 4. Temperature dependence of soliton density in the incommensurate and commensurate phases. The incommensurate-commensurate transition temperature is estimated from this plot to be 92 °C.

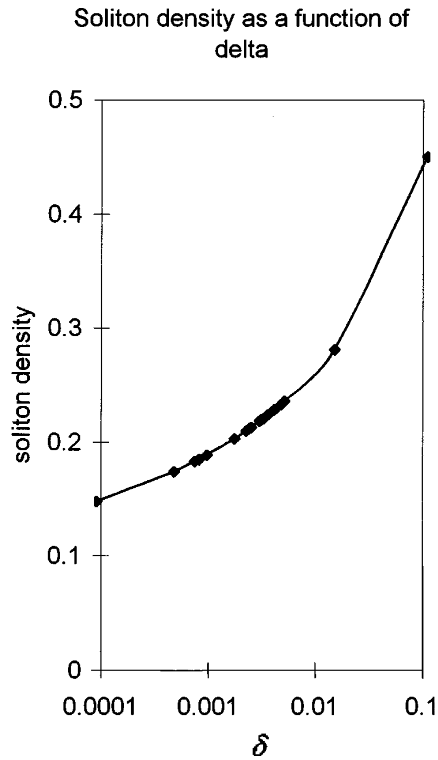

FIG. 5. Relation between the soliton density n_s and the parameter δ. The values of δ are extracted by the simulations of the spectra, and the values of n_s are calculated by Eq. (9).

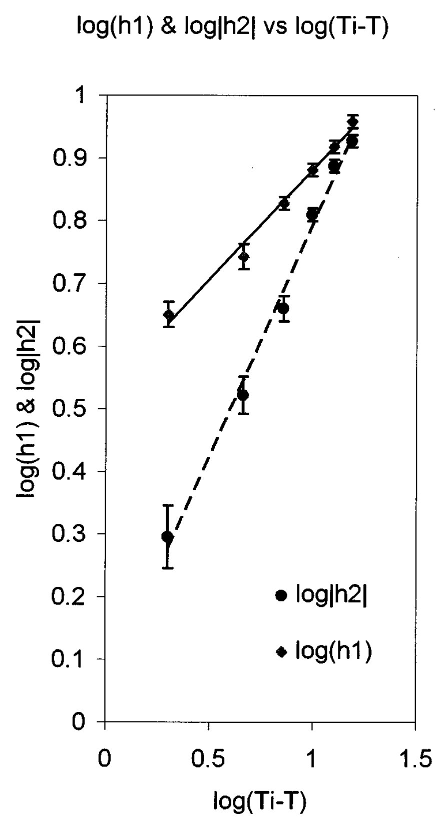

FIG. 6. Logarithm to base 10 of parameters h_1, h_2 plotted as function of the logarithm of the temperature difference $T_1 - T$, showing the power-law behavior. The exponent β is determined from the slope to be 0.36±0.03.

due mainly to the uncertainty in measuring T_I, which is of the order of $\pm 0.5\,°C$.

Since we have established a multisoliton picture for the incommensurate phase, we would like to find the phase of the commensurate domains. In the commensurate domains, we have, approximately

$$\frac{d\phi}{dx} \approx 0. \tag{14}$$

It follows immediately from Eq. (5) or (8)

$$\phi = \pm \frac{\pi}{4}, \pm \frac{3\pi}{4}. \tag{15}$$

CONCLUSION

Our results confirm the existence of a one-dimensionally modulated incommensurate phase in $(NH_4)_2ZnCl_4$. The form and temperature dependence of the ESR spectra are in excellent agreement with the predictions of the phase-soliton theory. The parameters h_1 and h_2 determining the variation of resonant magnetic field show a power-law behavior as a function of temperature, from which the average value [Eqs. (12) and (13)] of the critical exponent β was found to be 0.36 ± 0.03. Here, the value of β for $(NH_4)_2ZnCl_4$ has been measured and reported. The value of the critical exponent that we determined for this particular crystal and the values determined by other researches for other crystals of the A_2BX_4 family and some crystals not belonging to the A_2BX_4 family[10] are in very good agreement with the X-Y model.[2,5,8] Our results also show that the soliton density does not change significantly during the whole incommensurate phase and this behavior is quite different from that of Rb_2ZnCl_4.[4] With a better temperature controller, our future work on this particular crystal will focus on its critical behavior, especially on the temperature dependence of soliton density at temperatures very close to incommensurate-commensurate phase transition.

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