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ESR investigations of incommensurate Rb_2ZnCl_4:Mn^{2+}

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ESR spectra of Mn^{2+} probe have been studied in incommensurate rubidium zinc chloride monocrystals. It has been shown that temperature dependence of the resonance fields of ESR fine transition M_S=3/2↔5/2 can be satisfactorily described based on the simple "local" model. ESR line position data confirm non-classical character of the Rb_2ZnCl_4 critical properties, corresponding to 3D XY Heizenberg model.

Key words: *incommensurate phase transition, electron spin resonance.*

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1. Introduction

Rubidium zinc chloride Rb_2ZnCl_4 is one of the most intensively investigated compounds with A_2BX_4 formulae [1]. Below T_i=303 K Rb_2ZnCl_4 undergoes the phase transition from high temperature paraelectric phase (space group $D_{2h}^{16}-\mathrm{Pnam}$) to the incommensurate phase with wave vector of structural modulation $\mathbf{q_i}$=(1/3-δ)$\mathbf{a}*$ directed along $\mathbf{a}$ axis [2]. As it is well known a considerable progress in studying the incommensurate phases has been achieved by using radiospectroscopic techniques and in particular via ESR of Mn^{2+} probe in Rb_2ZnCl_4 crystals [3]. Investigations of the orientational diagrams of the ESR fine structure have shown that Mn^{2+} centers, substituting Zn^{2+} ions, are localized in chloride tetrahedra. Detection of the forbidden hyperfine doublets ($\Delta m_J = \pm\, 1$) on passing through paraelectric-incommensurate phase transition unequivocally indicates that Mn^{2+} is an appropriate paramagnetic probe and it is very sensitive to ($ZnCl_4$) group rotations associated with incommensurate structural modulation [4].

The purpose of this paper is to present the results of ESR measurements performed on the monocrystals Rb_2ZnCl_4 doped with Mn^{2+} probe. The samples studied have been cut out from the monocrystals grown by Chokhralskii method. ESR spectra have been measured on cooling run by using the conventional X-band spectrometer. The temperature of the samples was regulated by means of a standard nitrogen

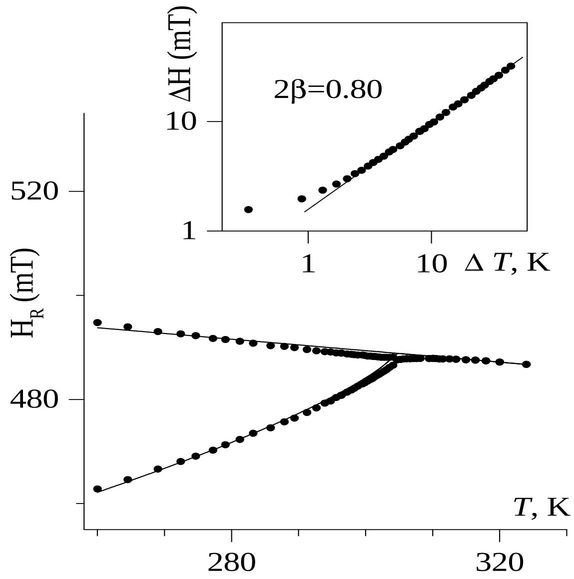

Figure 1. Resonance fields of hyperfine line m_J=5/2, M_S=3/2↔5/2 around T_i at $\mathbf{H} \parallel \mathbf{a}$. Solid lines are calculated using (2). In the insert: splitting between singularities ΔH vs. $\Delta T = (T_i - T)$ in a log-log scale.

gas flow cryostat providing the temperature stabilisation within 0.1 K during the ESR spectrum recording.

2. Temperature dependence of Mn^{2+} ESR spectra

It is well known that below T_i the single lines of magnetic resonance transform into inhomogeneously broadened spectra restricted by edge singularity peaks [5]. The singular line shape, having been observed in a number of incommensurate materials, reflects the dependence of the ESR signal position at the phase of incommensurate distortion. In the high temperature interval of incommensurate phase the plane wave limit represents a reasonable approximation. If displacements of all neighbours within the range of the probe are in phase then incommensurate distortion at the given lattice site can be expressed in the simple "local" form $U = \rho \cos \varphi(z)$ [5,6]. Here the amplitude ρ is assumed spatially independent whereas the phase φ varies linearly along the modulation axis $\varphi = q_i z + \varphi_0$. According to neutron scattering data [2], the phase shift between Cl^- ions, forming $(ZnCl_4)$ tetrahedra, does not exceed $\sim 2^0$ just below T_i and further decreases on cooling. So, it may be expected, that displacements of Mn^{2+} nearest neighbouring Cl^- ions are nearly in phase and, hence, "local" approximation [5,6] should be well adapted to the description of ESR spectra in the temperature region adjoining T_i. In this case the resonance fields can be expanded in powers of the local order parameter U

$$H_R = H_0 + aU + \frac{1}{2}bU^2 + ... = H_0 + A\Delta T^\beta \cos\varphi + \frac{1}{2}B\Delta T^{2\beta} \cos^2\varphi;$$

$$\Delta T = (T_i - T),\ \rho \sim \Delta T^{\beta},\ A \sim a,\ B \sim b. \tag{1}$$

Here H_0 corresponds to the line position in high temperature paraelectric phase. Expansion parameters in (1) depend on the paramagnetic ion location in the unit cell and on the direction of the external magnetic field **H** with respect to the crystallographic axes. If **H** is applied along (or perpendicular to) the local symmetry elements vanishing at the phase transition, the coefficients at linear term in (1) should be equal to zero. In this case on cooling below T_i the single line splits into the spectrum edged by two singularity peaks. Their positions are determined by condition $|\mathrm{d}H_R/\mathrm{d}\varphi| = 0$ [5] and in accordance with (1) are given by

$$\begin{aligned} H_{Q1} &= H_0 && (\varphi = \pm\pi/2), \\ H_{Q2} &= H_0 + \frac{1}{2}B\Delta T^{2\beta} && (\varphi = 0, \pi). \end{aligned} \tag{2}$$

So, H_{Q1} corresponds to the line position in paraelectric phase, whereas singularity H_{Q2} shifts from H_0 proportionally to the order parameter amplitude squared $\rho^2 \sim \Delta T^{2\beta}$. If the applied magnetic field destroys the symmetry elements vanishing at T_i, the linear term in (1) is allowed by symmetry. In the case of dominant linear contribution to the resonance fields two singularities are observed below T_i at

$$\begin{aligned} H_{L1} &= H_0 - A\Delta T^{\beta} + \frac{1}{2}B\Delta T^{2\beta} && (\varphi = 0), \\ H_{L2} &= H_0 + A\Delta T^{\beta} + \frac{1}{2}B\Delta T^{2\beta} && (\varphi = \pi). \end{aligned} \tag{3}$$

It has to be noted that if $A < |B|$, the third singularity should appear at the temperature independent position

$$H_{LQ} = H_0 - \frac{A^2}{2B}.$$

The high field Mn^{2+} hyperfine sextuplet corresponding to electron transition M_S=3/2↔5/2 has been measured in the temperature range of T_i for the following orientations of static magnetic field: i) **H** || **a** and ii) **H** deviated from **a** to **c** axis up to 7°. Above T_i the line position has been determined by simulation of the spectral contour by convolution of lorentzian function with gaussian distribution. In the incommensurate phase it was assumed that individual paramagnetic center gave the lorentzian shaped signal, the position of which depends on the amplitude and phase of incommensurate displacements according to (1).

The temperature dependence of the resonance fields of low field hyperfine component (m_J=5/2) for orientation i) **H** || **a** is represented in figure 1. In high temperature phase the hyperfine line weakly shifts toward high fields. Below T_i=304.4 K the single line splits into singularity spectrum. On cooling, high field singularity nearly continues the thermal drift of line position in paraphase, whereas another singularity considerably shifts to low fields. Since in the paraelectric phase (**ab**) represents the mirror plane for paramagnetic centers point symmetry group, the linear term

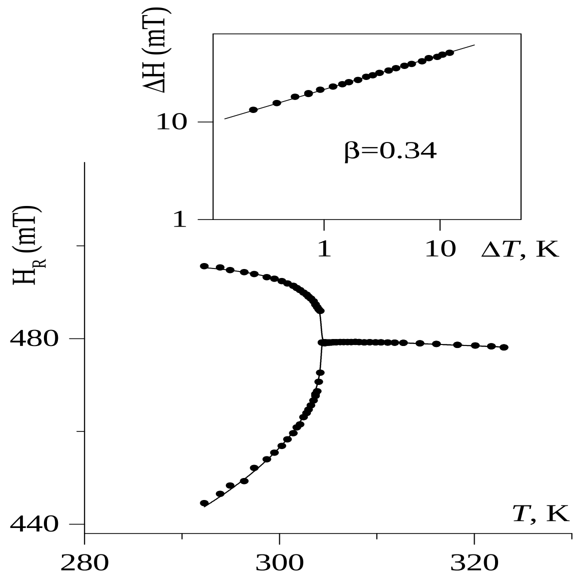

Figure 2. Temperature dependence of resonance fields at the deviated orientation $\angle\mathbf{H},\mathbf{a}$=7°, $\mathbf{H}\perp\mathbf{b}$. Solid lines are calculated using (3). In the insert: ΔH vs. ΔT in a double logarithmic scale.

in expansion (1) vanishes for the orientation considered. Hence quadratic coupling between resonance fields and the order parameter is realized and line positions have to be described by expressions (2). The distance between singularities according to (2) equals $\Delta H = H_{Q2} - H_{Q1} = (B/2)\Delta T^{2\beta}$. The singularity splitting ΔH versus $(T_i - T)$ is represented in the insert to figure 1 in a double logarithmic scale. It can be seen that for $(T_i - T) > 3.5$ K the experimental behaviour corresponds to the straight line with the mean slope of 0.80±0.01. The theoretical dependencies, calculated using (2) and taking into account the H_0 thermal drift, the estimated index value 2β=0.80 and parameter B_1=–3.28 mTK$^{-2\beta}$ (A_1=0), are represented in figure 1 by solid lines. Following the arguments presented in [7,8], the deviation of calculated curves from experimental dependencies observed around T_i may be ascribed to the mean square fluctuations contributing to the line position.

For the deviated orientation ii) $\angle\mathbf{H},\mathbf{a}$=7° the resonance fields measured in the range of T_i are represented in the figure 2. In this case, the applied magnetic field breaks the mirror plane (**ab**), the linear term in (1) is allowed by symmetry and provides the dominant contribution to the resonance fields. The singularity splitting, in accordance with (3) equal to $\Delta H = H_{L2} - H_{L1}$ =$2A\Delta T^{\beta}$, is plotted in the insert to the figure 2 in a log-log scale. The experimental dependence can be approximated by a straight line with the mean slope β=0.34±0.01. The solid lines depicted in the figure 2 are calculated using (3) with parameters A_2=10.86 mTK$^{-\beta}$, B_2=–4.02 mTK$^{-2\beta}$.

The data obtained and represented in figures 1,2 show that resonance fields of the ESR fine sextuplet M_S=3/2↔5/2 can be satisfactorily described by expansion (1) based on the “local” approximation [5]. Nevertheless, the tendency of high field singularity temperature behaviour (figure 1) allows us to assume that at lower temperatures "non-local" effects would become noticeable. One may suppose that superposition of rotation and twist of chloride tetrahedra would result in "non-locality" of interaction [9].

The order parameter critical index estimated from the linear singularity splitting β=0.34 is consistent with the previous NMR [10] and ESR [11,12] data. This value is very close to the theoretical exponent of 3D XY Heizenberg model. It is remarkable that within the experimental accuracy the value of critical exponent determined in the case of "quadratic" coupling (2β=0.80) noticeably exceeds the doubled β value derived from linearly splitted singularity spectra. This departure qualitatively agrees with NMR results [10] and may be attributed to the secondary order parameters having totally different character of critical behaviour in comparison with the primary lattice distortion. As it has been pointed out in [13], the contribution of the secondary order parameters can alter the values of critical indexes measured experimentally.

3. Conclusions

It has been shown that temperature behaviour of the Mn^{2+} electron transition M_S=3/2$\leftrightarrow$5/2 in high temperature interval of Rb_2 Zn Cl_4 incommensurate phase can be satisfactorily described based on the simple "local" approximation [5]. In accordance with order parameter dimensionality (n=2) the determined value of critical index β corresponds to 3D XY Heizenberg model. Non-coincidence of the critical indexes obtained for the cases of linear and quadratic coupling of resonance fields with the order parameter confirms a non-classical character of the rubidium zinc chloride critical properties.

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ЕПР дослідження несумірних кристалів $Rb_2ZnCl_4:Mn^{2+}$

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Проведено вивчення ЕПР спектрів Mn^{2+} у несумірній фазі монокристалів тетрахлорцинкату рубідію. Показано, що температурна поведінка резонансних полів електронного переходу M_S=3/2↔5/2 може бути описана в рамках простої “локальної” моделі. Температурні залежності положення резонансних ліній підтверджують некласичний характер властивостей Rb_2ZnCl_4 відповідний до 3D XY моделі Гейзенберга.

Ключові слова: *неспівмірний фазовий перехід, електронний парамагнітний резонанс*

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