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ESR study of the Prussian blue analogue $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$

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Abstract

We performed electron spin resonance (ESR) studies of the mixed valence Prussian blue analogue, $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ in a wide frequency (9.5–319 GHz) and temperature (3.5–300 K) interval. Evidence for the proposed high-temperature Mn^{2+} ($S = \frac{5}{2}$)–NC– Fe^{3+} ($S = \frac{1}{2}$) to low-temperature Mn^{3+} ($S = 2$)–NC– Fe^{2+} ($S = 0$) internal charge transfer has been detected: a characteristic reduction of $\chi_{\text{ESR}}T$ on cooling from room temperature to 100 K, a particular frequency dependence of the room temperature ESR linewidth, and the temperature dependence of the ESR linewidth. Short-range magnetic correlations, reflected in a large broadening and dramatic shift of the ESR signal develop just above $T_C = 10$ K. Below T_C , both the linewidth and the shift in position mimic the temperature dependence of the order parameter. In a quench experiment T_C was reduced by 3 K. The observed ferromagnetic ordering arises from Mn^{3+} ($S = 2$) moments in the low-temperature electronic configuration.

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1. Introduction

Photo-switchable materials have emerged in recent years as very promising systems for optical memories and/or numerical displays [1]. They are usually transition metal complexes that can switch between a low spin (LS) and a high spin (HS) state upon an external perturbation. Additionally one may combine different transition metal ions in mixed valence compounds in order to tailor their magnetic properties. Prussian blue analogues with the general formula $\text{A}_x\text{M}_y\text{M}'^{\text{II}}[\text{M}'^{\text{III}}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ represent such model systems. Here A is an alkali metal cation, and M and M' are di- and trivalent transition metal cations. The flip between electronic states can occur with temperature or pressure changes or under light illumination.

The $\text{RbMn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ system [2–4] has proven a versatile test system for thermo- and photo-induced electron transfer, i.e. the high-temperature Mn^{2+} ($S = \frac{5}{2}$)–NC– Fe^{2+} ($S = \frac{1}{2}$) transforms into the low-temperature Mn^{3+} ($S = 2$)–NC– Fe^{3+} ($S = 0$) electronic state. The low temperature spin configuration orders ferromagnetically below 12 K. The ferromagnetic order is associated with the alignment of the Jahn–Teller active Mn^{3+} ($S = 2$) moments [5]. In addition, the characteristics of both the thermo- and photo-induced electron transfer can be sensitively tuned by introducing $[\text{Fe}^{\text{III}}(\text{CN})_6]$ vacancies in the crystal structure, resulting in systems with stoichiometry, $\text{Rb}_x\text{Mn}_{(3-x)/2}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($x < 1$). For instance, $\text{Rb}_{0.7}\text{Mn}_{1.15}[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ has at room temperature a face-centred cubic structure ($\text{Fm}\bar{3}\text{m}$, $a = 10.54314(4)$ Å) with a transition-metal configuration HS Mn^{2+} ($S = \frac{5}{2}$)–NC–LS Fe^{2+} ($S = \frac{1}{2}$) analogous to $\text{RbMn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ and displays a rich variety of electronic and spin

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transformations with X-ray irradiation as a function of time and temperature [6].

In this work we focus on the related $[\text{Fe}^{\text{III}}(\text{CN})_6]$ defective system, $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ [6] and have studied the possible electronic and spin transitions by temperature dependent electron spin resonance (ESR) spectroscopy in the frequency range between 9.5 and 319 GHz.

2. Experimental details

The sample used in the present work was prepared according to the procedure described in Ref. [6] and was characterized by elemental and thermogravimetric analysis, synchrotron X-ray powder diffraction and SQUID magnetometry.

Approximately 5 mg of the $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ powder was sealed in a quartz capillary for ESR measurements. X-band ($\nu_L = 9.5$ GHz) and Q-band ($\nu_L = 34.5$ GHz) ESR experiments were performed with a home-built spectrometer using Varian X- and Q-band bridges. An Oxford ESR 900 continuous flow liquid He cryogenic system ensured temperature stability better than 0.1 K. High frequency continuous wave ESR measurements were performed at the high-magnetic field facility of the NHMFL [7].

3. Results and discussion

Room temperature ESR spectra measured in as-prepared samples can be fitted for all resonant frequencies with a simple Lorentzian lineshape. In X-band, the ESR signal has a g -factor, $g = 2.0199$ and a peak-to-peak linewidth, $\Delta H_{\text{pp}} = 220$ G. However, the frequency dependence of ΔH_{pp} shows unusual behaviour (Fig. 1). The linewidth first decreases, reaching a shallow minimum at

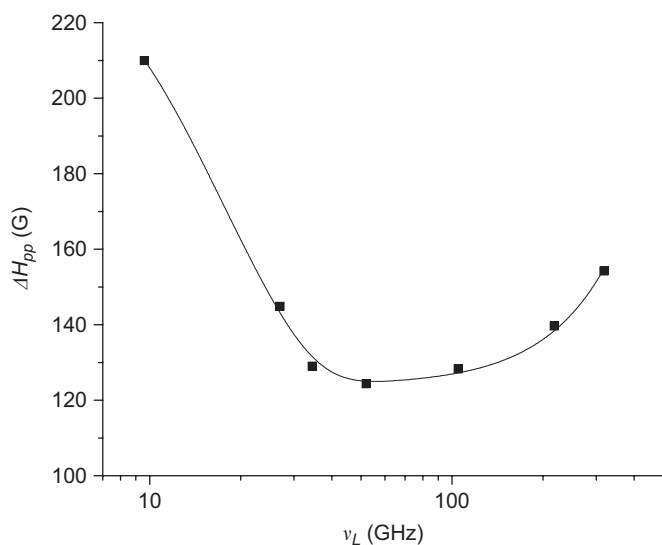


Fig. 1. Frequency dependence of the peak-to-peak EPR linewidth for $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ measured at room temperature.

$\nu_L = 52$ GHz, where $\Delta H_{\text{pp}} = 124$ G, and then it starts to increase with increasing frequency.

The broadening of the ESR spectra at high resonant frequencies ($\nu \geq 50$ GHz) probably reflects the presence of two different strongly coupled spin centres (Mn^{2+} and Fe^{3+}) with different g -factors. In the case of strong exchange, the linewidth varies as

$$\Delta H_{\text{pp}} \approx \frac{(H_{C1} - H_{C2})^2}{H_e} + \Delta H_0. \quad (1)$$

Here H_{C1} and H_{C2} are the resonance fields for the two different centres determined by their g_i -factor values: $H_{Ci} = h\nu/g_i\mu_B$, H_e is an exchange field proportional to the Mn^{2+} – Fe^{3+} exchange coupling constant J , and ΔH_0 is an exchange independent contribution to the linewidth. Eq. (1) can satisfactorily describe the experimental data at high frequencies but it fails below 50 GHz. In order to explain the anomalous low-frequency behaviour, one needs to consider some kind of spin dynamics. As a probable candidate we invoke a dynamic competition between the high-temperature (Mn^{2+} – NC – Fe^{3+}) and the low-temperature (Mn^{3+} – NC – Fe^{2+}) configurations. This suggestion is consistent with the behaviour of the magnetic susceptibility, which shows the presence of thermal hysteretic behaviour in χT in this temperature range [8].

Additional evidence for the occurrence of an internal charge transfer in $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ is provided by the temperature dependence of the X-band ESR susceptibility, χ_{ESR} . Calibrated ESR susceptibility is at room temperature only 6.4×10^{-4} emu/mol, i.e. only 3.5% of expected spin susceptibility. Measured signal is thus likely to be associated with the defects in the structure, which are however still sensitive to transformations as it will be described below. χ_{ESR} deviates from a simple Curie–Weiss law, $\chi = C/(T-\theta)$ over the entire temperature range, while $\chi_{\text{ESR}}T$ gradually decreases from $\chi_{\text{ESR}}T = 0.19$ (1) emu K/mol at room temperature to $\chi_{\text{ESR}}T = 0.17$ (1) emu K/mol at 200 K (Fig. 2). On cooling below 200 K, $\chi_{\text{ESR}}T$ is nearly temperature independent down to 40 K.

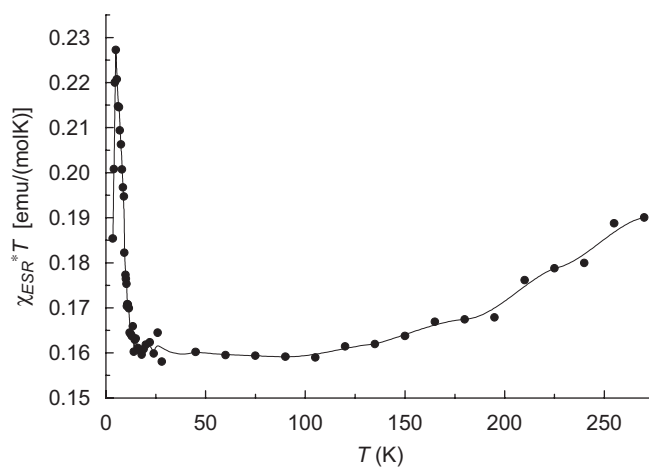


Fig. 2. Temperature dependence of the X-band $\chi_{\text{ESR}}T$ measured on cooling.

This behaviour resembles the temperature dependence of the SQUID magnetic susceptibility data [8], which can be explained in terms of thermally induced transformation between two competing electronic configurations: a high-temperature HS Mn^{2+} ($S = \frac{5}{2}$)–NC–LS Fe^{3+} ($S = \frac{1}{2}$) and a low-temperature HS Mn^{3+} ($S = 2$)–NC–LS Fe^{2+} ($S = 0$). We emphasize that in the ESR experiments we can detect only the high-temperature electronic states, as both the low-temperature Mn^{3+} and Fe^{2+} centres are beyond the reach of the X-band ESR experiments. Fe^{2+} has a spin $S = 0$ and is ESR silent. On the other hand, the Jahn–Teller active Mn^{3+} ($S = 2$) ion is expected to have a huge zero-field splitting. The allowed ESR transitions for this ion are thus expected at very large fields, well outside our experimental setup. Nevertheless their presence will be indirectly reflected in the development of the spin correlation functions, which determine the temperature dependence of the ESR linewidth.

The variation of $\chi_{\text{ESR}}T$ below 20 K is typical for a magnetic system undergoing collective magnetic ordering at $T_C = 10$ K. In analogy to $\text{RbMn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$, we interpret the observed transition as arising from the magnetic ordering of the Mn^{3+} ($S = 2$) moments mediated by the orthogonal orbitals of the intervening Fe^{2+} ($S = 0$) centres.

The temperature response of the X-band ESR linewidth (Fig. 3) confirms the above observations. We first note a small anomaly in the temperature range between room temperature and 100 K, i.e. in the same temperature interval where $\chi_{\text{ESR}}T$ decreases by $\sim 16\%$ (Fig. 2). Once the low-temperature electronic configuration is established, a nearly linear decrease of the linewidth with decreasing temperature is observed below 100 K. Such behaviour is typical of the evolution of the spin correlations and is frequently encountered in magnetic systems. The linewidth reaches a minimum of 228 G at around 13 K. Below 13 K the signal starts to broaden substantially. Nearly saturated value of 312 G is obtained below ~ 8 K. We notice that the temperature dependence of the linewidth is reminiscent of

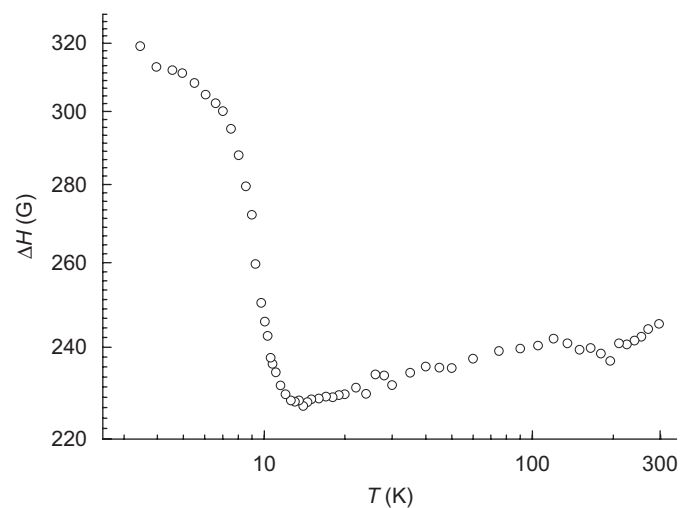


Fig. 3. Temperature dependence of the ESR peak-to-peak linewidth measured in X-band experiment.

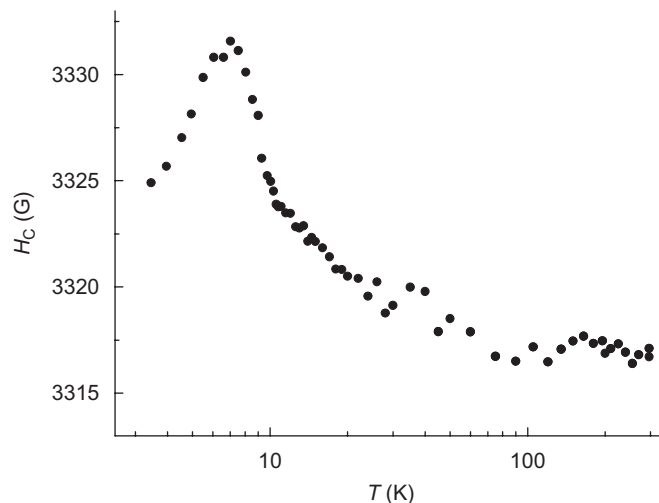


Fig. 4. Temperature dependence of the centre of the line measured in the X-band ESR experiment taken on cooling.

the temperature dependence of the magnetization and can thus serve as a measure of the order parameter.

These conclusions are also supported by the temperature dependence of the centre of the X-band spectra (Fig. 4). The centre of the line is almost temperature independent down to 100 K. At lower temperatures close to T_C a progressive shift towards higher fields is observed, presumably reflecting short-range order effects [9]. Below T_C the centre of the line dramatically shifts from 3332 to 3325 G between 10 and 7 K. We again note that the shift is reminiscent to the order parameter given by the magnetization. The shift below T_C is thus a result of the evolution of the demagnetizing fields, i.e.

$$H_{\text{res}}(T) = H_0 - N \cdot M(T). \quad (2)$$

Here N is the demagnetizing factor dependent on the particle shape and $M(T)$ is the temperature-dependent particle magnetization.

We also examined the effect of the cooling rate on the magnetic properties. Our sample was quenched from room temperature to 40 K in a pre-cooled cryostat. Given the slow dynamics of the charge transfer, this cooling protocol froze the system in the high-temperature electronic state. A significant shift of the magnetic transition temperature from $T_C = 10$ to 7 K and a reduction of the order parameter as measured by the broadening of the X-band ESR line have been observed. These observations suggest that the concentration of the low-temperature HS Mn^{3+} ($S = 2$)–NC–LS Fe^{2+} ($S = 0$) units is relevant for the magnetic ordering in our sample.

4. Conclusions

We have studied the stability of the $\text{Rb}_{0.8}\text{Mn}_{1.1}[\text{Fe}(\text{CN})_6] \cdot \text{D}_2\text{O}$ electronic and magnetic structures under different thermal treatments by ESR spectroscopy in a wide frequency range. The X-band ESR results indicate

incomplete transformations between high-temperature HS Mn^{2+} ($S = \frac{5}{2}$)–NC–LS Fe^{3+} ($S = \frac{1}{2}$) and low-temperature HS Mn^{3+} ($S = 2$)–NC–LS Fe^{2+} ($S = 0$) electronic configurations. Development of spin correlations in the vicinity of $T_C = 10$ K is reflected in particular on the change in the linewidth and the shift of the ESR signal. The magnetic transition is associated with the ferromagnetic ordering of Mn^{3+} ($S = 2$) magnetic moments in the low-temperature magnetic structure.

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