

A variable temperature EPR study of Mn^{2+} -doped $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ single crystal at 170 GHz: Zero-field splitting parameter and its absolute sign

Sushil K. Misra^{a,*}, Serguei I. Andronenko^a, Prem Chand^b, Keith A. Earle^c,
Sergei V. Paschenko^{c,1}, Jack H. Freed^c

^a Physics Department, Concordia University, Montreal, Que., Canada H3G 1M8

^b Physics Department, Indian Institute of Technology, Kanpur-208016, UP, India

^c Baker laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853-1301, USA

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Abstract

EPR measurements have been carried out on a single crystal of Mn^{2+} -doped $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ at 170-GHz in the temperature range of 312–4.2 K. The spectra have been analyzed (i) to estimate the spin-Hamiltonian parameters; (ii) to study the temperature variation of the zero-field splitting (ZFS) parameter; (iii) to confirm the negative absolute sign of the ZFS parameter unequivocally from the temperature-dependent relative intensities of hyperfine sextets at temperatures below 10 K; and (iv) to detect the occurrence of a structural phase transition at 4.35 K from the change in the structure of the EPR lines with temperature below 10 K.

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1. Introduction

A variety of guest ions can be introduced into the lattices of ammonium halides. Hetero-valent transition metal ions have been of particular interest for optical, EPR and ENDOR measurements to study the nature of defect centers and the mechanism for charge compensation. In particular, the S ground state Mn^{2+} ion has been widely used as an EPR probe. We summarize the relevant published results on EPR in alkali halides here. The first EPR investigation of the Mn^{2+} ion in ammonium chloride was reported by Abe and Shirai in 1960

[1]. A variable temperature EPR study of the Mn^{2+} ion in an NH_4Cl crystal was carried out by Zaripov and Chirkin [2] down to 1.43 K. An EPR study of Mn^{2+} in NH_4I was also reported by Chand and Upreti [3]. The unusually large value of the second order zero-field-splitting (ZFS) parameter, b_2^0 (also referred to as D), is responsible for many unusual features in EPR spectra at low frequencies: X-band (~ 9.5 GHz) and Q-band (~ 35 GHz). In the series of alkali halides, the mixed crystal $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ doped with the Mn^{2+} ion, was recently studied by multifrequency EPR by Misra et al. [4] at X-band (~ 9.6 GHz), Q-band (~ 36 GHz) and FIR (far infrared)-band (249.9 GHz). The X-, Q- and FIR band measurements were performed at 295/125 K, at 295/77, and 253 K, respectively. The multifrequency data yielded very precise values of the spin-Hamiltonian parameters. A considerable simplification

* Corresponding author. Fax: +1 514 848 2828.

E-mail address: skmisra@vax2.concordia.ca (S.K. Misra).

¹ Present address: Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, USA.

of the Mn^{2+} spectrum was found at the very high frequency FIR band. Although it was possible to rotate the crystal at all frequencies studied, sufficient range of magnetic field required to observe all the Mn^{2+} transitions for the orientation of the external magnetic field (\mathbf{B}) along the magnetic Z -axis was not available at Q- and FIR-bands, which required 0.5–1.9 and 8.2–9.6 T, respectively. In addition, it was not possible to perform a low-temperature study at the FIR band due to the lack of a stable low-temperature cryostat suitable for the narrow-bore magnet used for the experiment. Thus, the absolute sign of the ZFS parameter b_2^0 could not be determined from the relative intensity of lines at liquid-helium temperature in the same fashion as accomplished by Chemerisov et al. [5] by using high-field EPR at low temperatures. Also, the occurrence of a possible low temperature phase transition could not be investigated.

Recently, a 170 GHz induction-mode EPR spectrometer was implemented at Cornell University using a new wide-bore (89 mm) 9.2 T superconducting magnet (Magnex) with a 4–330 K variable temperature accessory (Janis), allowing measurements down to 4 K. A goniometer suitable for this magnet/cryostat combination is under development. Nevertheless, taking advantage of the presence of three magnetically inequivalent, but physically equivalent, Mn^{2+} centers in the unit cell of the cubic $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ crystal, it became possible to observe simultaneously the Mn^{2+} EPR spectra for orientations of $\mathbf{B} \parallel Z$ and the X/Y magnetic axes. This follows from symmetry considerations. When the crystal is oriented such that one of its cubic edges is parallel to \mathbf{B} , one of the three magnetically inequivalent Mn^{2+} centers in the crystal has its magnetic Z -axis parallel to \mathbf{B} , whereas the other two have their X and Y magnetic axes parallel to \mathbf{B} . Due to axial symmetry around the respective magnetic Z -axis, the spectra for $\mathbf{B} \parallel X$ and $\mathbf{B} \parallel Y$ are the same. (Hereafter, these equivalent axes will be referred to as X/Y axes.) Taken together, the three Mn^{2+} ions in the unit cell, thus provide EPR spectra for $\mathbf{B} \parallel Z$, X axes for this particular orientation of the crystal with respect to the magnetic field. Moreover, at 170 GHz, the full Mn^{2+} EPR spectrum can be observed as it only requires a magnetic field scan of 6–7 T, which is well below the maximum magnetic field (9.2 T) of the superconducting magnet used in the experiment.

This paper is a sequel to [4], supplementing the previously published results by (i) estimating the values of the spin-Hamiltonian parameters at several temperatures in the liquid-helium range; (ii) studying the temperature variation of the ZFS parameter b_2^0 ; (iii) determining unequivocally the absolute sign of the ZFS b_2^0 from the relative intensity of EPR lines at several temperatures between 4.2 and 312 K; and (iv) detecting the occurrence of a structural phase transition hitherto not reported at about 4.35 K. The details of the previously

published Mn^{2+} EPR studies on NH_4Cl and NH_4I , sample preparation, crystal structure, details of higher temperature phase transitions and the procedure to determine the values of spin-Hamiltonian parameters have already been described in [4]. Only the new results will be included in the present communication.

2. Experimental results

The 170-GHz spectrometer uses a bridge based on quasi-optical design techniques [6]. This bridge is the third generation of a broadband bridge that exploits polarization-coding techniques to minimize transmitter feed-through [7]. It achieves broadband capability by using broadband, polarization-preserving corrugated waveguide to propagate the millimeter waves from the bridge to the probe-head and back. The detected signal may be observed in either of two modes: induction or reflection. The induction mode was used in the study presented here; it consists of an excitation in one polarization state and observation of the EPR signal in the cross-polarized, or orthogonal, polarization state. The cross-polarized EPR signal is generated by the preferential absorption of one circularly polarized component of the incident millimeter wave by the EPR phenomenon. In the absence of polarization-perturbing imperfections in the quasi-optical bridge, the signal in the orthogonal polarization state is due solely to EPR mechanisms. In practice, the following mechanisms reduce the signal-to-noise ratio of the cross-polarized EPR signal: bridge component misalignment and termination mismatches, polarization perturbations arising from the use of off-axis ellipsoidal mirrors, presence of the sample, imperfections in the resonator alignment and tuning, and magnetic field modulation induced microphonics. (A more complete discussion is found in [6,8]). Cryogenic temperatures were achieved using a commercial cryostat (Janis) with a feedback loop for temperature control. Temperatures between 4.2 and 330 K were readily obtained. For the work reported here, a range of temperatures, with primary emphasis on the range 4.2–100 K was achieved with good temperature stability using helium gas flow.

The 170-GHz EPR spectra for Mn^{2+} in an $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ crystal, with one of the cubic edges of the crystal being oriented along the external magnetic field, as observed at 312, 30, 10, 6, 4.45, and 4.29 K, are exhibited in Fig. 1. Since there exist three magnetically inequivalent Mn^{2+} centers in the crystal, the spectra corresponding to $\mathbf{B} \parallel Z$ and X/Y magnetic axes are observed at the same time as explained in Section 1. An inspection of Fig. 1 reveals that the lowest-, central-, and highest-field hyperfine sextets for $\mathbf{B} \parallel X/Y$ -axis overlap the three inner sextets for $\mathbf{B} \parallel Z$ -axis.

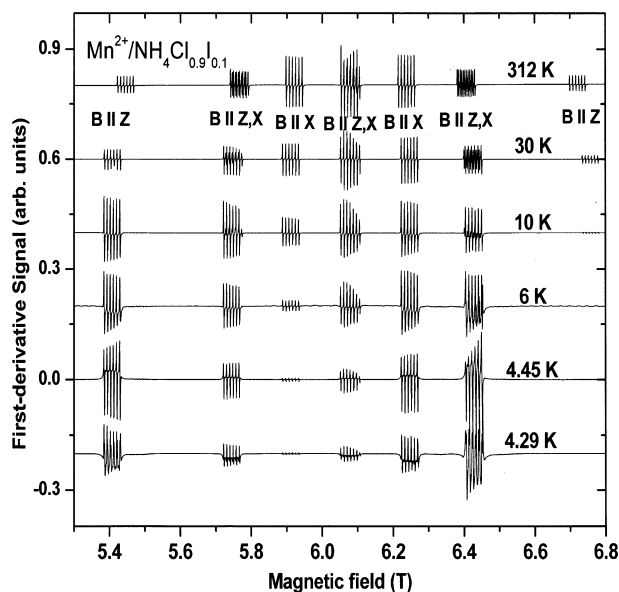


Fig. 1. First-derivative EPR spectra observed for Mn^{2+} in $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ single crystal at 170 GHz at various temperatures. The two sets of spectra for Mn^{2+} centers with their Z and X/Y axes parallel to \mathbf{B} are also indicated.

3. Spin-Hamiltonian parameters

Resonance fields for orientations of \mathbf{B} along two perpendicular magnetic Z and X/Y axes were fitted simultaneously using a rigorous least-squares fitting procedure as described in [4] to estimate the values of spin-Hamiltonian parameters. For temperatures less than 10 K, and for $\mathbf{B} \parallel Z$ magnetic axis, only the three lowest hyperfine sextets were observed as the intensity of the two highest-field sextets diminished almost completely, as described in the next section. On the other hand, for $\mathbf{B} \parallel X/Y$ -axes all the five hyperfine sextets were observed, although in this case the intensity of the lowest-field sextet is very small. Further, as expected for S-state ions, the g -value for Mn^{2+} in $\text{NH}_4\text{I}_{0.1}\text{Cl}_{0.9}$ was found to be close to the free-electron value (2.0023), and did not ex-

hibit any significant temperature dependence. Likewise, the hyperfine interaction parameter (A) also exhibited no significant temperature dependence down to 4.29 K.

The fine-structure resonant line positions for $\mathbf{B} \parallel Z$, X/Y -axes were fitted to the following spin Hamiltonian [4]: $H = \mu_B g \mathbf{S} \cdot \mathbf{B} + b_2^0 O_2^0 + b_4^0 O_4^0$. The values of the parameters as estimated by fitting line positions are listed in Table 1. (At 4.29 K, the average line positions of the split lines were fitted to evaluate parameters.) The crystal field about the Mn^{2+} ion is found to be axial between 300 and 4.45 K, just above the phase-transition temperature. The temperature dependence of the ZFS parameter b_2^0 is shown in Fig. 2. Its magnitude decreases by ca. 5% between 300 and 4.45 K.

4. Absolute sign of the ZFS parameter b_2^0

In the present study, the sign of the b_2^0 parameter has been unequivocally confirmed to be negative by directly observing the change in the relative intensities of the various fine structure sextets below 30 K. (Previously, the sign of the parameter b_2^0 in $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ was assumed to be negative [4], the same as that determined in NH_4Cl from the relative intensities of Mn^{2+} EPR lines at 1.43 K by Zaripov and Chirkin [2].) As seen clearly in Fig. 1, the transitions occurring at higher field become progressively less intense compared to those occurring at lower field with lowering temperature for $\mathbf{B} \parallel Z$ -axis, and vice versa for $\mathbf{B} \parallel X/Y$ -axis [9]. This is due to the fact that the large values of the magnetic fields required to observe EPR resonances at 170 GHz result in widely different, transition-dependent Boltzmann factors at low temperatures that determine the populations of the Mn^{2+} energy levels. As the intensity of a transition is proportional to the difference in the populations of the energy levels participating in the resonance, there was observed an almost complete suppression of the highest field transition in the spectrum for $\mathbf{B} \parallel Z$ -axis below 10 K accompanied by the same observation for the lowest

Table 1

The values of the ZFS parameters b_2^0 and b_4^0 of the Mn^{2+} ion in $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ crystal at various temperatures

Temperature (K)	b_2^0 (GHz)	b_4^0 (GHz)	n	RMSL
312	-4.534 ± 0.001	0.006 ± 0.002	10	0.012
297	-4.551 ± 0.001	0.007 ± 0.002	10	0.021
30	-4.781 ± 0.001	0.008 ± 0.002	10	0.015
10	-4.804 ± 0.001	0.008 ± 0.002	10	0.013
6	-4.804 ± 0.001	0.007 ± 0.002	8	0.017
4.45	-4.803 ± 0.001	0.008 ± 0.002	8	0.017
4.29	-4.802 ± 0.001	0.006 ± 0.002	8	0.019

Here, the root-mean-square deviation between the FIR frequency and the energy level separation per line RMSL (GHz) is defined to be equal to $(\text{SMD}/n)^{1/2}$, where $\text{SMD} (\text{GHz}^2) \equiv \sum_i (\Delta E_i - \nu)^2$ and n is number of hyperfine sextets fitted simultaneously. In the expression for SMD, ΔE_i is the calculated energy difference in GHz between the levels participating in resonance for the i th line position and ν is the FIR frequency in GHz. At all temperatures: $g = 1.9997 \pm 0.0001$ and $A = -0.2489 \pm 0.0003$. The misorientation angle in the ZX plane as fitted to data was found to be less than 0.5° in all cases. For comparison, as listed in [4], at 295 K, $g = 1.9997$ and b_2^0 (GHz) = -4.538 as determined at 253 K from 249.9 GHz spectra, whereas $g = 1.9997$ and b_2^0 (GHz) = -4.563 as determined at 295 K from $X + Q + \text{FIR}$ bands spectra.

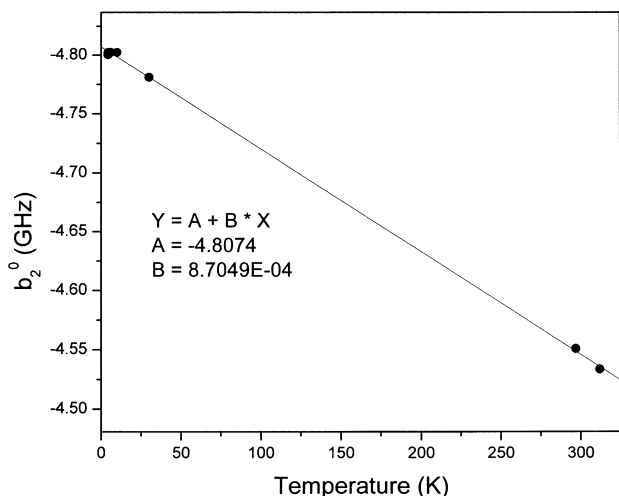


Fig. 2. Variation of the ZFS parameter b_2^0 with temperature. The straight line represents a linear fit to the values.

field hyperfine sextet for the spectrum for $\mathbf{B} \parallel X/Y$ -axis below 4.4 K. Different behaviors of the intensities of the EPR lines for the orientations of the magnetic field along the Z and X/Y axes of the Mn^{2+} center occur because the sign of the parameter b_2^0 changes from negative to positive in transforming from the reference frame with the magnetic Z -axis parallel to \mathbf{B} to the reference frame with the magnetic X/Y -axis parallel to \mathbf{B} , with \mathbf{B} defining the axis of quantization [10]. The relative intensities of the highest- and lowest- field sextets depend on the relative populations of the fine-structure Mn^{2+} energy levels in $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$. For example, the population ratios of the lowest- and highest-field sextets for $\mathbf{B} \parallel Z$ -axis at various temperatures as calculated from the Boltzmann populations are 1.1, 2.4, and 36 at 312, 30, and 10 K, respectively.

5. Phase transition at 4.35 K

The spectra observed for the lowest field sextet of the Mn^{2+} center for $\mathbf{B} \parallel Z$ -axis at temperatures 10, 6, 4.45, and 4.29 K, are shown in Fig. 3. Splitting of the EPR lines was observed unambiguously in the lowest-field sextet at 4.29 K. It indicates the occurrence of a structural phase transition at $T_c = 4.35 \pm 0.5$ K. Each line was clearly split by ca. 15 G, significantly larger than the EPR linewidth of ca. 10 G. This splitting is only observed at very high frequency, e.g., 170 GHz, reported in the present study. At X-band [4], only broadening of the EPR lines was observed, rendering the phase transition unobservable. As one sees from Table 1, the value of the ZFS parameter also changed somewhat at 4.29 K, below T_c , as compared to that at 4.45 K, above T_c . Specifically, the absolute value of the parameter b_2^0 decreases as compared to that at 4.45 K. Enough data are not available to study the nature of this transition.

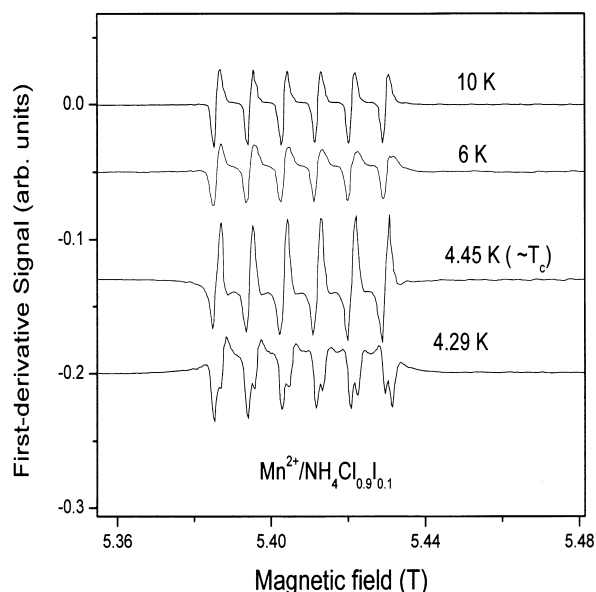


Fig. 3. Variation of the first-derivative EPR spectrum for the lowest field sextet for Mn^{2+} in $\text{NH}_4\text{Cl}_{0.9}\text{I}_{0.1}$ at temperatures ≤ 10 K clearly indicating the occurrence of a structural phase transition at 4.35 ± 0.15 K.

The only statement that can be made is that below 4.45 K the point symmetry seen by the Mn^{2+} ion is such that the inversion symmetry prevalent above this temperature is lost so that the two ions in the unit cell become slightly physically inequivalent. This results in splitting of the EPR lines.

6. Concluding remarks

The present investigations have been carried out to study the variation of the ZFS parameter b_2^0 down to 4 K and to determine unequivocally the absolute sign of b_2^0 to be negative. The very-high-frequency EPR study presented here offered the following advantages over those at low-frequency EPR. (i) The Mn^{2+} EPR spectrum was easy to interpret [4,11]. (ii) Due to the much enhanced relative intensity changes at low temperatures, it became possible to identify unambiguously the transitions belonging to the three magnetically inequivalent Mn^{2+} centers, even though they overlapped each other. (iii) A phase transition was detected at 4.35 ± 0.5 K, not possible at X-band because of lack of sufficiently resolved spectrum. This phase transition has not been reported previously, and warrants further investigation using other techniques, e.g., X-ray crystallography.

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