

EPR study of guanidine zinc sulphate crystals

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Abstract. X-band electron paramagnetic resonance (EPR) investigations of Mn^{2+} -doped guanidine zinc sulphate $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$ – abbreviated as GZS – are presented. The EPR spectrum in the temperature range 273–393 K exhibits a group of five fine structure transitions each splits into six hyperfine components. The angular variation of EPR spectra reveals the presence of only one magnetic complex, which correspond to one distinct site of Mn^{2+} ions in the crystal lattice. From the observed EPR spectrum, the spin-Hamiltonian parameters have been evaluated. The variation of zero-field splitting (ZFS) parameter, intensity and line width with temperature are measured and discussed.

Key words: electron paramagnetic resonance (EPR) • zero-field splitting (ZFS) • transition ions in crystals

Introduction

Guanidine derivatives and salts are biologically important due to the presence of functional amino groups and often exhibit interesting physical properties [2–4, 11]. There are known ferroelectric crystals containing guanidinium monovalent cations, namely $[\text{C}(\text{NH}_2)_3]\text{Me}(\text{AO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $[\text{C}(\text{NH}_2)_3]_4\text{SO}_4\text{X}_2$ families [9, 18]. The structural studies of a quite large family of hydrated guanidinium double sulphates of divalent transition metals were presented recently [5]. Guanidine zinc sulphate $[\text{C}(\text{NH}_2)_3]_2\text{Zn}(\text{SO}_4)_2$ (abbreviated as GZS) is the only one known anhydrous crystal with the complex crystal structure [5, 10]. At room temperature, the crystal is tetragonal with space group of and four formula units in unit cell. The network of zinc and sulphate ions constitutes the main feature of the structure where sulphate ions are arranged tetrahedrally around the zinc ions. The GZS was supposed to undergo a phase transition at elevated temperatures [8]. However, DTA and DTG studies [17] did not find any phase transition and decomposition of the crystal up to about 600 K. Recently, on the basis of the calorimetric and dielectric studies it was found that the GZS crystals exhibit the second order structural phase transition at 178 K [4].

In the present paper we report the EPR measurements manganese-doped GZS crystals performed in the X-band in the temperature range from room temperature (RT) down to 150 K. The rotation patterns of the spectra are also studied in detail and described. So far, the magnetic resonance methods have not been employed in studies of this system.

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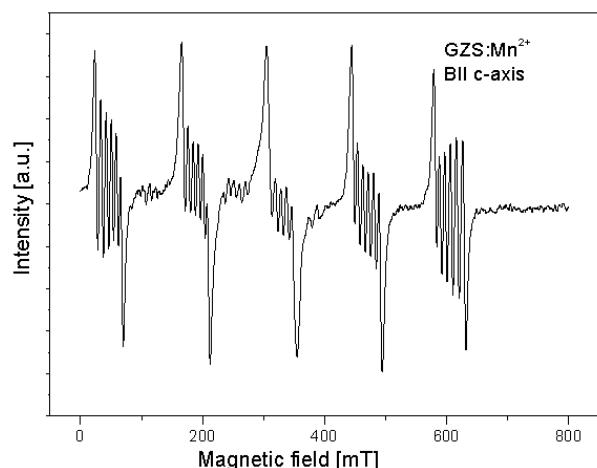


Fig. 1. The EPR spectrum of Mn^{2+} in GZS single crystal, when the external magnetic field is along the c-axis in the plane at 393 K.

Experimental

Manganese-doped GZS single crystals were grown from a water solution of stoichiometric quantities of guanidinium sulphate ($[\text{C}(\text{NH}_2)_3]_2\text{SO}_4$) and zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) with a small excess of sulphuric acid (H_2SO_4) by the slow evaporation method at a constant temperature of 305 K. About 0.5% of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was added to the resultant solution as paramagnetic impurity during the growth. The divalent manganese ions with the electron configuration $3d^5$ substitute statistically at zinc sites. The paramagnetic manganese ions are very sensitive probes on the slight changes of their environment.

EPR measurements were performed in the X-band (9.5 GHz) using standard spectrometers, equipped with a sample cavity of TE102 mode and 100 kHz modulation. The spectra were recorded with a spectrometer, which was interfaced with a microcomputer via USB port for controlling the instrument, acquisition and display of the acquired spectra.

A goniometer sample holder provided the rotation of the sample ($\pm 0.5^\circ$) about the given vertical axis. The Cartesian laboratory axes xyz , chosen for the angle-dependent measurements were related to the tetragonal crystallographic axes (a, b, c) as follows: ($x \parallel a, y \parallel b, z \parallel c$) [10]. The spectra were recorded by varying the orientation of the external magnetic field in a given plane at 5° angle intervals. The temperature of the sample was established by regulating the temperature of the cooling gas streaming around the sample, was controlled by a Wildmad cryostat with an accuracy of relative and absolute temperature values of 0.1 and 1 K, respectively.

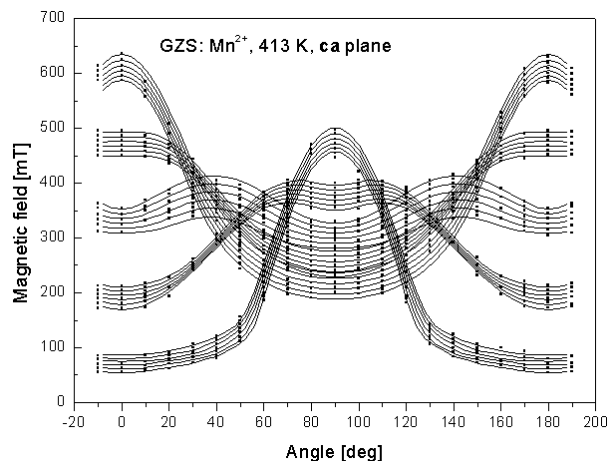


Fig. 2. The angular dependence of the Mn^{2+} EPR spectra at 393 K in GZS at X-band. Points represent the experimental data and the solid lines show the fitted results with the parameters given in Table 1.

Results and discussion

The ground state of Mn^{2+} ion, with a $3d^5$ configuration, splits into three Kramer's doublets ($\pm 5/2$, $\pm 3/2$, and $\pm 1/2$) in a low symmetry crystalline field, which are further split in the presence of the applied magnetic field. These splitting give rise to five fine structure transitions. Each fine structure transition is split into six hyperfine components due to the ^{55}Mn hyperfine coupling giving in all 30 allowed transitions. The observed EPR spectrum of Mn^{2+} ions doped in GZS single crystals, when the external magnetic field is along the c-axis in the plane at 393 K is shown in Fig. 1. Angular dependences of the EPR spectra were studied at a temperature $T = 393$ K in three mutually orthogonal planes namely ab , bc and ac planes in steps of 5° .

The rotation pattern taken in the ca plane in GZS is shown in Fig. 2. The angular variation behaviour of the spectrum in the bc plane is similar to that of ac plane.

In the ab plane the EPR spectrum does not undergo change with the rotation of the crystal. So, the angular variation and the spin-Hamiltonian parameters suggest that the local symmetry around Mn^{2+} ion is an axial one.

The EPR spectra have been analyzed using the spin-Hamiltonian (SH) of the form [1, 13]

$$(1) \quad \hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60} b_4^0 O_4^0 + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S}$$

where the first term represents the electronic Zeeman, the second and third terms represent the contributions of zero-field splitting (ZFS) and the fourth terms represent the hyperfine interaction term. Other symbols have their usual meanings.

Table 1. The fitted spin Hamiltonian parameters for Mn^{2+} in GZS and some other Mn^{2+} doped diamagnetic host crystals for comparison. The ZFS and hyperfine parameters are in (10^{-4} cm^{-1})

Crystal	Temperature (K)	g	b_2^0	b_2^2	b_4^0	A	Reference
GZS	RT	2.003	702	0	4	-83	Present work
GZS	393	2.005	653	0	5	-85	Present work
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	300	2.002	435	-70	5	-92	[14]
$\text{KZnClO}_4 \cdot 7\text{H}_2\text{O}$	343	2.012	-312	53	11.2	-80	[12]

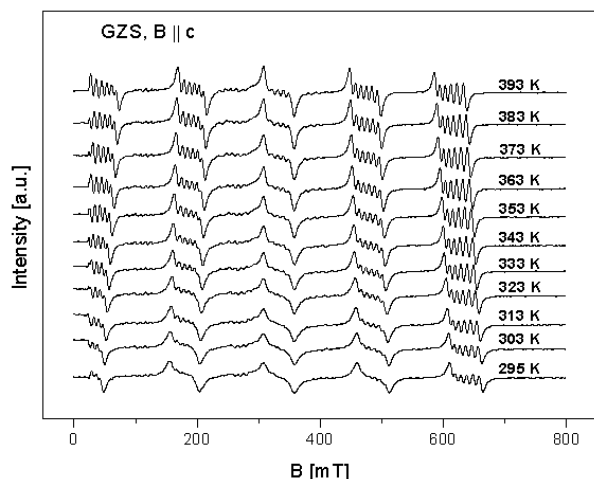


Fig. 3. Temperature dependence of the Mn^{2+} EPR spectrum in the GZS measured at X-band with the magnetic field B direction parallel to the c -axis in the ac plane.

The SH parameters were calculated with exact diagonalization of the energy matrices using a computer program provided by Grachev [7]. The SH parameters obtained at RT and 393 K are listed in Table 1. The g value and hyperfine constant A are isotropic namely $g = g_{\parallel} = g_{\perp}$ and $A = A_{\parallel} = A_{\perp}$ within the experimental error.

EPR spectra of Mn^{2+} ions doped in GZS single crystals were also recorded at different temperatures from 293 to 393 K, when the magnetic field is along the c -axis in the ac plane. Figure 3 shows the EPR spectra of Mn^{2+} doped in GZS single crystals at different temperature ions when the magnetic field is along the c -axis in the ac plane.

As the temperature is increased from room temperature, the intensity of all the hyperfine lines slightly increases and the linewidth decreases. As the temperature of the crystal is lowered from room temperature, the width of the resonance lines increases and a nearly broadened out spectrum is observed at 160 K. The changes of the intensity and the linewidth of $|-1/2m\rangle \rightarrow |-3/2m\rangle$ transition lines are presented in Figs. 4 and 5, respectively.

The spin-Hamiltonian parameters were evaluated at different temperatures and there is no appreciable temperature effect on g and A values. The ZFS param-

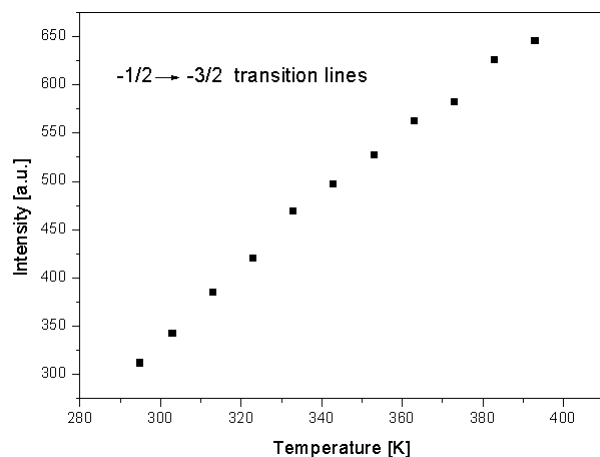


Fig. 4. Temperature dependence of the intensity of $|-1/2m\rangle \rightarrow |-3/2m\rangle$ transition lines for Mn^{2+} ions in GZS single crystals.

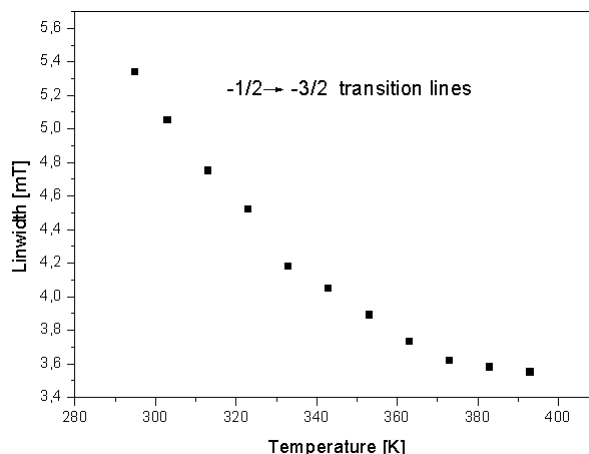


Fig. 5. Temperature dependence of the linewidth of $|-1/2m\rangle \rightarrow |-3/2m\rangle$ transition lines for Mn^{2+} ions in GZS single crystals.

eters b_2^0 are found to be very sensitive to temperatures. Figure 6 shows the temperature variation of b_2^0 from 293 to 393 K. In the present work, it is observed that b_2^0 value increases with decreasing temperature.

The observed increase in ZFS constant (b_2^0) with decreasing of temperature usually is attributed to the thermal contraction of the lattice. Similar observations were reported for Mn^{2+} ions elsewhere [6, 15].

It would be of interest to determine the absolute sign of b_2^0 . The sign of b_2^0 can be assigned with respect to A by following the separation between the hyperfine structure lines from the low field to the high field. If the separation between the hyperfine lines in the low field is greater than the high field, then the ratio b_2^0/A becomes positive or b_2^0/A will be negative for the reverse case. Here, in the present case, the separation between the hyperfine lines increases from lower field to higher field, which indicates that b_2^0/A is negative. Because A is invariably negative for all high spin Mn^{2+} compounds due to the core polarization of inner orbitals of Mn^{2+} , it is inferred that the sign of b_2^0 for Mn^{2+} in GZS is positive.

It is also possible to get information about the nature of bonding between the manganese ion and its immediate surroundings by the determination of the hyperfine splitting constant A . The relation between the hyperfine splitting constant A and the local bonding of Mn^{2+} ions

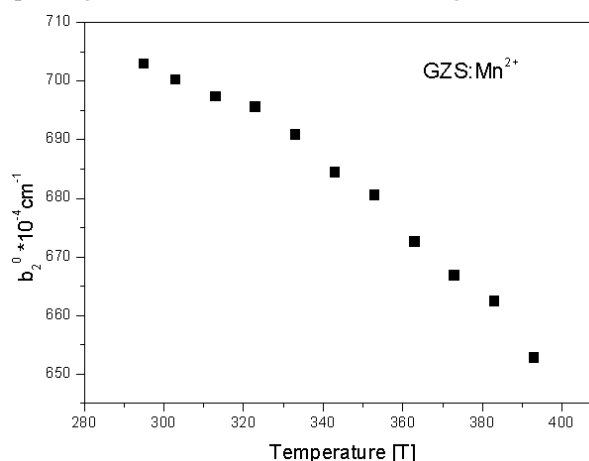


Fig. 6. Temperature dependence of zero field splitting parameter for Mn^{2+} ions in GZS single crystals.

and the nearest neighbour ligands is usually analyzed by plotting A vs. the Pauling covalency parameter [16]. From the curve, for the hyperfine splitting constant $A = -85 \times 10^{-4} \text{ cm}^{-1}$, we can say that the bonding present in Mn^{2+} - doped GZS single crystal is moderately ionic.

Conclusions

EPR spectra of Mn^{2+} ions in zinc guanidinium sulphate (GZS) single crystals have been studied in the temperature range 160–393 K. The detailed study of the GZS: Mn^{2+} single crystal reveals that Mn^{2+} ions enter substitutionally at the Zn^{2+} site. The evaluated spin Hamiltonian parameters reflect the axial symmetry of the crystal lattice. From the hyperfine splitting constant A , it can be concluded that bonding between the paramagnetic ion and the ligands is moderately ionic. The observed increase in zero-field splitting constant (b_2^0) with decreasing temperature has been attributed to the thermal contraction of the lattice. At low temperatures, the line width increases and the EPR spectrum completely broadens out at 160 K.

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