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Characterization of Mn^{2+} doped tetramethylammoniumtetrachlorozincate single crystal using EPR and optical absorption

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Abstract

Studies of fine and hyperfine structures of paramagnetic resonance spectra in single crystals of Mn^{2+}: tetramethylammoniumtetrachlorozincate are reported. As sufficient numbers of lines were not obtained at room temperature, measurements were done at liquid nitrogen temperature (77 K). The Mn^{2+} spin Hamiltonian parameters are evaluated employing a large number of resonant line positions observed for various orientations of the external magnetic field. The values of the zero field parameters that give good fit to the observed EPR spectra are obtained. The values of different parameters are: $g = 1.9834 \pm 0.0002$, $\mathcal{A} = (105 \pm 2) \times 10^{-4}\,cm^{-1}$, $\mathcal{B} = (100 \pm 2) \times 10^{-4}\,cm^{-1}$, $D = (349 \pm 2) \times 10^{-4}\,cm^{-1}$, $E = (106 \pm 2) \times 10^{-4}\,cm^{-1}$ and $a = (21 \pm 1) \times 10^{-4}\,cm^{-1}$. The percentage of covalency of the metal–ligand bond has also been determined. From the optical absorption study, the lattice distortion is suggested. The observed bands are assigned as transitions from the $^6A_{1g}(S)$ ground state to various excited quartet levels of Mn^{2+} ion in a cubic crystalline field. The electron repulsion parameters (B and C) and crystal field parameters (D_q and α) providing a good fit to the observed optical spectra are evaluated and the values are: $B = 737\,cm^{-1}$, $C = 2322\,cm^{-1}$, $D_q = 670\,cm^{-1}$ and $\alpha = 76\,cm^{-1}$. The considerable decrease in the values of B and C parameters from free ion values ($B = 960\,cm^{-1}$, $C = 3325\,cm^{-1}$) has indicated that there exists a fair amount of covalent bonding between the central metal ion and the ligand. On the basis of deviations $\Delta g = g - 2.0023$ it has been ascertained whether electrons are transferred to or from the central ion by the action of bonding.

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Keywords: Spin Hamiltonian; Optical absorption; Electron repulsion parameters; Crystal field; Bonding parameters

1. Introduction

EPR is a spectroscopic technique used to obtain microscopic chemical and physical information about molecule. EPR and optical absorption have been used as investigative tool for the study of transition metal ions and radicals in solid materials, to obtain information about symmetry of crystalline electric field and associated distortion in the lattice [1–4]. When paramagnetic ions are introduced in host lattices local distortion will take place due to mismatch of paramagnetic ion size to that of host ions. The optical study provides energy level ordering of different orbital levels of paramagnetic ion and crystalline field strength in the host lattice [5].

Divalent manganese is of interest among paramagnetic complexes of iron group [6–10]. The shell of 3d-electrons in Mn^{2+} ion responsible for paramagnetism is just half-filled by five electrons of Mn^{2+} ion and the resultant orbital angular momentum is zero. The ground state is ^6S. The crystalline electric field can affect the electron spins only through high order interactions so that spins are almost completely free to orient themselves in an external magnetic field [11]. In the present study the EPR and optical study of Mn^{2+} doped tetramethylammoniumtetrachlorozincate are reported to obtain information whether Mn^{2+} ion enters the lattice substitutionally or interstitially and to obtain structure of energy levels of Mn^{2+} ion. Further the data obtained are used to get information about the nature of bonding of metal ion with its different ligands.

2. Crystal structure

The crystal structure of tetramethylammoniumtetrachlorozincate was studied by Wiesner et al. [12]. The space group is P_{nma}

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with $Z=4$. The cell dimensions are $a=12.276$ Å, $b=8.998$ Å, $c=15.541$ Å. There is some disordering in the orientation of both the $[MCl_4]^{2-}$ and the $[N(CH_3)_4]^{+}$ tetrahedra.

3. Experimental

Single crystals of tetramethylammoniumtetrachlorozincate (TMATC-Zn) are grown at room temperature by slow evaporation of an aqueous solution containing tetramethylammonium chloride and zinc chloride in stoichiometric proportions. For Mn^{2+} doped crystals 0.1 wt% of manganese chloride is added to the mixture. Good transparent crystals grow in about 15 days. The EPR spectra are recorded using X-band Varian E-112 EPR spectrometer with 100 kHz field modulations. As sufficient number of lines were not obtained at room temperature, spectra were recorded at liquid nitrogen temperature .The single crystals are mounted at the end of a quartz-rod using quick-fix and crystal rotations are performed along the three mutually perpendicular axes *a*, *b* and *c* using a goniometer. The magnetic field was measured using a Varian flux meter and a proton probe with the help of a Hewlett-Packard frequency counter. The optical absorption spectra were recorded on a Unicam-5625

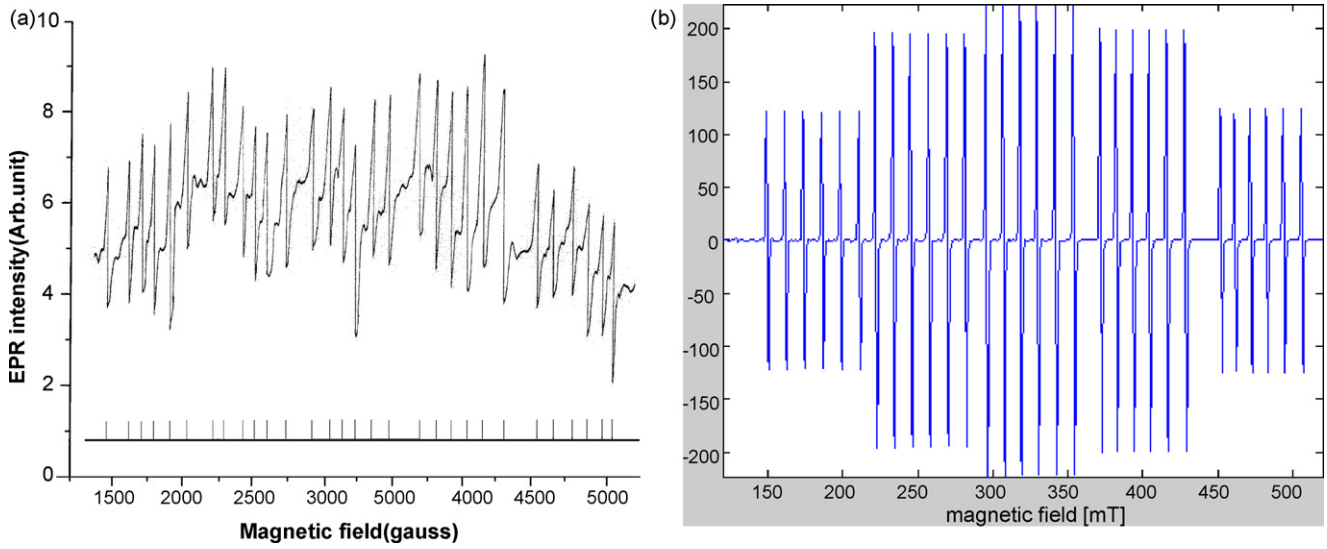

Fig. 1. (a) EPR spectrum of Mn^{2+} doped TMATC-Zn single crystal for magnetic field B parallel to the '*b*' axis. (b) Simulated EPR spectrum of Mn^{2+} doped TMATC-Zn single crystal for magnetic field ***B*** parallel to the '*b*' axis (microwave frequency 9.11 GHz).

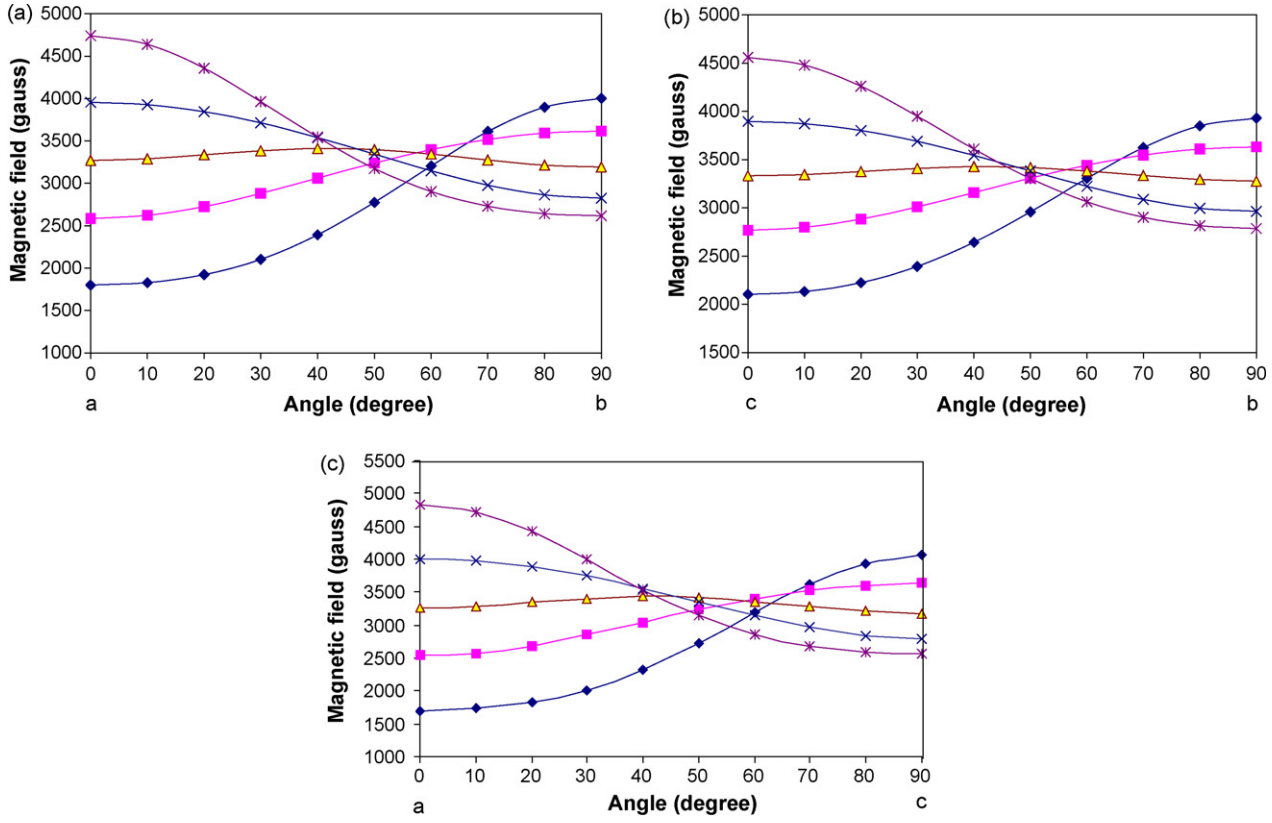

Fig. 2. Angular variation of the fine structure of Mn^{2+} doped TMATC-Zn single crystal in the (a) *ab* plane; (b) *cb* plane; (c) ac plane.