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Local structure determination of Mn^{2+} in $CaCl_2$:Mn^{2+} by optical spectroscopy

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Abstract

Excitation and emission spectra of Mn^{2+} ions in calcium chloride have been studied using the photoluminescence technique. From a crystal-field analysis of the excitation spectrum is inferred that the Mn^{2+} ion occupies the Ca^{2+} cation site forming octahedral $MnCl_6^{4-}$ complexes. A ligand inward relaxation around the Mn^{2+} is noticed as a consequence of smaller ionic radius of Mn^{2+} than that of host cation. This investigation supports the usefulness of crystal-field spectra for obtaining information on the local structure of impurity ions in ionic lattices.

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1. Introduction

A good characterization of an active ion within an ionic lattice requires to know the local structure around the ion, that is the neighbourhood ions, site symmetry and bond distances, since the optical and magnetic properties of doped crystals depend significantly on the complex formed by the impurity ion and its nearest neighbours. Moreover, the R distance between the impurity ion and its nearest neighbours can be very different from the R_0 distance corresponding to the perfect lattice. The R distance has could be determined from a crystal-field analysis of excitation optical spectra [1–4], which has resulted to be the same (within the experimental error) as those previously determined by other techniques, such as the extended X-ray absorption fine structure (EXAFS) [1], and electron paramagnetic resonance (EPR) or electron nuclear double resonance (ENDOR) spectroscopy [5,6] through measuring the isotropic superhyperfine constant. In addition, an accuracy of the order 10^{-3} Å has been achieved with such an optical procedure in contrast with that (10^{-2} Å) achieved with EXAFS [1], in spite of its continuous improvements in the last years.

The goal of the present work is to investigate by means of optical spectroscopy the local structure of Mn^{2+} ions (site symmetry and bond distances) in $CaCl_2$:Mn^{2+}. The interest in this crystal, with orthorhombic structure, lies in that excitation spectroscopy performed on this phosphor containing Mn^{2+} ions has revealed that such ions can be excited free of photoconductive process, and hence, their excitation bands have been attributed to Mn^{2+} internal transitions of the $3d^5$ configuration [7]. The site symmetry of Mn^{2+} in $CaCl_2$ could be determined from an analysis of its crystal-field transitions. The Mn^{2+}–Cl^- distance was obtained from the R-dependence of $10Dq$ ligand field splitting considering a KR^{-n} variation [1–4].

The $10Dq$ magnitude of Mn^{2+} in $CaCl_2$:Mn^{2+} was determined from an analysis of its excitation spectrum

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using the procedure developed by Curie et al. [8]. This procedure includes the covalent effects as well as the Racah–Trees or polarization and seniority corrections. Such covalent effects are taken into account through the covalent reduce Racah parameters B' and C' which represent a measure of the metal–ligand covalency. Thus, in octahedral coordination metal–ligand complexes the simultaneous reduction of the B and C Racah parameters is brought out by the N_t^4 factor [9]: $B' = BN_t^4$ and $C' = CN_t^4$. The N_e normalization factor, which is associated with the Racah parameter reduction in tetrahedral coordination complexes, is related with N_t through the Koide–Pryce covalency parameter ε [10]: $N_e = N_t(1-\varepsilon)^{1/2}$. If such a reduction of B and C or (N_t and N_e) with respect to the free ion values, $B = 918\,\mathrm{cm}^{-1}$ and $C = 3273\,\mathrm{cm}^{-1}$ ($N_t = N_e = 1$) [8] is due to a bonding effect, then the electronic wavefunction within the complex is no longer a pure Mn^{2+} orbital, but rather a molecular orbital wavefunction, which can be expressed as:

$$|t_{2g}\rangle = N_t(|d_{xy,yz,xz}\rangle - \lambda_t|L_t\rangle) \quad \text{and}$$
$$|e_g\rangle = N_e(|d_{3z2-r2,x2-y2}\rangle - \lambda_e|L_e\rangle), \tag{1}$$

where d and L refer to the metal d-orbitals and the p- and s-orbital linear combinations, respectively. In this way, N_t and N_e are important bonding parameters, which require to be evaluated in order to obtain some information on the bonding ionicity, since weaker the mixing of metal and ligand functions, N_t and N_e become close to 1.

2. Experimental

A colourless single crystal of $CaCl_2$ doped with Mn^{2+} ions was grown in our laboratory in an evacuated quartz ampoule using the Bridgman technique. Starting materials of very high purity were previously dehydrated by slow heating to 280 °C under mechanical vacuum. Due to the quite hygroscopic character of calcium chloride, the optical spectroscopy of $CaCl_2$:Mn^{2+} was performed with the crystal contained into an evacuated quartz ampoule to avoid adsorption and inclusion of water. The very small oscillator strengths ($\sim 10^{-8}$) of the Mn^{2+} ion crystal-field transitions make difficult to detect photoluminescence spectra in crystals doped with low concentration of Mn^{2+}. Thus, the manganese concentration in the melt was around 3200 ppm, which was the lowest one so that the Mn^{2+} luminescence could be detected with our experimental equipment. The lowest concentration possible is employed to prevent dimer formation, as well migration processes and exchange interactions, which can significantly affect the optical spectra.

Emission and excitation spectra were obtained with the same experimental equipment described in [7]. The excitation spectra were not corrected for the photomultiplier response, since we were only concerned with the peak positions and not with the band intensities.

Lifetime measurements were performed exciting the crystal at 337 nm, with 10-ns pulses of a PRA LN120C UV laser. The resulting transient fluorescence signal was analysed with a 0.45 m Czerny–Turner monochromator, detected with a cooled Hamamatsu R943–03 photomultiplier tube, and processed by a Hewlett Packard model 54201A digitising oscilloscope.

3. Experimental results: analysis

Fig. 1 displays the excitation and emission spectra of Mn^{2+} ions in $CaCl_2$:Mn^{2+} at room-temperature (RT). The emission spectrum, obtained under excitation at 414 nm, consists of a broad band peaking at 578 nm, which is associated with the ${}^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ spin-forbidden transition of Mn^{2+} ions. In fact, the time dependence of this emission is exponential, with a lifetime of about 21 ms, which proves the forbidden character of the transition.

The excitation spectrum, monitored at 580 nm, was found to be very similar to those exhibited by Mn^{2+} ions in octahedral coordination chlorides, such as $CdCl_2$:Mn^{2+} [11], NH_4MnCl_3 [12], $KMgCl_3$:Mn^{2+} [1], $KCaCl_3$:Mn^{2+} [1] and $CsSrCl_3$:Mn^{2+} [1]. It consists of several absorption bands, which are associated with Mn^{2+} transitions from its ${}^6A_{1g}(S)$ ground state to the ${}^4T_{1g}(G)$, ${}^4T_{2g}(G)$, [${}^4A_{1g}(G)$, ${}^4E_g(G)$], ${}^4T_{2g}(D)$, ${}^4E_g(D)$, ${}^4T_{1g}(P)$, ${}^4A_{2g}(F)$, ${}^4T_{1g}(F)$ and ${}^4T_{2g}(F)$ levels, since excitation into any of these bands gives rise to the ${}^4T_{1g}(G) \rightarrow {}^6A_{1g}(S)$ emission. The same excitation spectra are obtained regardless of the monitored luminescence wavelength, which indicates that all Mn^{2+} ions are excited via the same excitation bands. The most

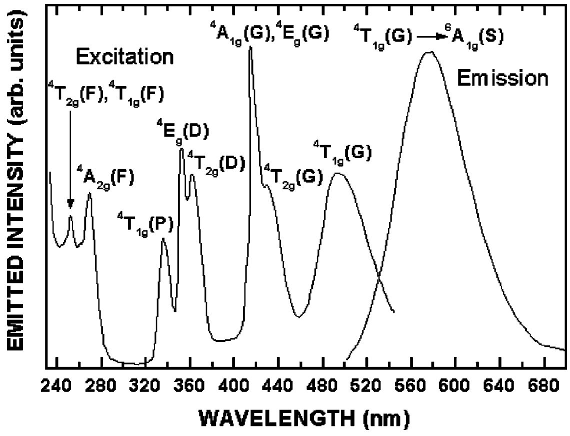

Fig. 1. RT emission and excitation spectra of $CaCl_2$:Mn^{2+}. The emission spectrum was obtained after excitation at 414 nm and the excitation one was monitored at 580 nm.