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# Exchange charge model calculations of crystal field parameters and crystal field energy levels for $[N(CH_3)_4]_2CoCl_4$ and $[N(CH_3)_4]_2MnCl_4$ single crystals

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**Abstract**

Complex study of $[N(CH_3)_4]_2MCl_4$ (M = Co, Mn) crystals (crystal growth, optical spectroscopy, crystal field analysis) is presented. Exchange charge model of crystal field was used to calculate the crystal field parameters (CFPs) and energy levels for both $Co^{2+}$ and $Mn^{2+}$ ions. Effects of the covalent bond formation between $Co^{2+}(Mn^{2+})$ and $Cl^-$ ions are treated from the point of view of overlap of the corresponding wave functions. Dependence of the CFPs values on the number of ions included into the crystal lattice summation was analyzed. Comparison between the calculated energy levels and corresponding absorption spectra is discussed; on the basis of the calculations, assignment of the absorption bands in the experimental spectra was done.



*Keywords:* Crystal growth; Light absorption and reflection

## 1. Introduction

$[N(CH_3)_4]_2MCl_4$ (M = Co, Mn) crystals (here and thereafter TMA-CoC and TMA-MnC, respectively) belong to a large group of materials whose general chemical formula can be written as $A_2BX_4$, where A = K, Rb, Cs, $NH_4$, $N(CH_3)_4$; B = Se, Zn, Co, Mn, Ni, Fe; X = I, Cl, Br, F [1–4]. Members of the above group can go through several phase transitions, both commensurate (C) and in-commensurate (IC); many studies devoted to their particular properties have been published in the literature so far. Specific properties of phase transitions were extensively analyzed using the high resolution X-ray diffraction [5–11], optical absorption studies [12–17], electron-spin resonance (ESR) technique [18–20], high-pressure experiments [21,22] and lattice vibration study [23]. In the previous work [24], the structure of the TMA-CoC and TMA-MnC crystals was analyzed using synchrotron radiation Laue diffraction. Electrical [25] and optical measurements [26,27] were also carried out to examine the electrical states of similar TMA-ZnC single crystals. The absorption edge in the mean crystallographic directions of TMA-MnC and TMA-CoC single crystals was studied in the normal para-electric phase (at 303 K). The optical transmittance and absorbance were measured [27] and used to estimate the absorption coefficient and the optical band gap $E_g$. In the present paper, we continue and extend our previous studies of the $A_2BX_4$ family members [24–31].

We report on the complex study of both TMA-CoC and TNA-MnC crystals, which includes crystal growth, absorption spectra measurements, and a wide range of topics initiated by application of the exchange charge model [32] of crystal field, namely, calculation of the overlap integrals between $Co^{2+}$–$Cl^-$ and $Mn^{2+}$–$Cl^-$ ions, estimation of the 3*d*-electron density moments, calculations of the crystal field parameters (CFP), analysis of their dependence on the number of ions accounted for in the lattice summations, diagonalization of the crystal field Hamiltonians for $Co^{2+}$ and $Mn^{2+}$ ions, and assignment of the observed

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absorption bands in terms of the calculated crystal field energy levels.

## 2. Crystal growth, crystal structure and absorption spectra measurements

Single crystals of TMA-MnC or TMA-CoC were grown by slow evaporation from the seeded super-saturated solutions prepared from a stoichiometric proportion of $N(CH_3)_4Cl$ and $MnCl_4$–$4H_2O$ (TMA-MnC) or $N(CH_3)_4Cl$ and $CoCl_4$ (TMA-CoC). The selected seeds were of good optical quality and showed the natural crystallographic faces. For the growth procedure, the seeds were suspended by a very thin nylon thread in a saturated solution at a fixed controlled temperature (303 K). To get a uniform crystallization, the seeds were rotated in two directions at the speed of 30 rpm. The described process of crystal growth took 4 weeks, after which single crystals of good optical quality were obtained. Typical sizes of the crystals were 2 cm × 2 cm × 3 cm. X-ray diffraction experiments were performed to confirm the structure of the samples. Good optical samples for the absorption measurements were cut in the cleave plane b and polished to a final thickness of 0.5 mm. Optical absorption measurements were performed using the Shimadzu 160A double beam automatic scanning spectrophotometers with spectral range from 200 to 900 nm. The spectra were recorded at 303 K.

Crystal structure of the tetramethylammonium tetrachlorocobaltate $(N(CH_3)_4)_2CoCl_4$ was described in Ref. [33]. It has an orthorhombic crystal structure, space group *Pnma* with the lattice constants $a = 12.276$ Å, $b = 9.001$ Å, and $c = 15.539$ Å. $Co^{2+}$ ions are surrounded by four $Cl^-$ ions, forming slightly distorted tetrahedron. Fig. 1 depicts one unit cell of TMA-CoC.

Crystal structure of TMA-MnC is similar to that one of TMA-CoC, and hence is not shown. It is also orthorhombic; space group *Pnma*, with lattice constants $a = 9.070$ Å, $b = 15.636$ Å, and $c = 12.345$ Å [34].

Optical absorption spectra of both crystals are due to the transitions between various states of 3*d*-electron configurations of 4-fold coordinated $Co^{2+}$ and $Mn^{2+}$ ions. Electrostatic interaction between 7*d*-electrons of $Co^{2+}$ gives rise to 8 LS terms ($^4$PF, $^2$PD$_1$D$_2$FGH), which in a crystal field can split into 50 energy levels, if the spin–orbit interaction is not considered. The ground term $^4$F is split in an ideal tetrahedral field into two orbital triplets $^4T_1$, $^4T_2$, and orbital singlet $^4A_2$ (being the ground level), whereas, the first excited term $^4$P is not split and remains to be the orbital triplet $^4T_1$. Optical spectra of tetrahedral $Co^{2+}$ consist of three wide bands associated with spin-allowed transitions from the $^4A_2$ ground state to the three above-mentioned spin-quartet states. Two lowest spin-allowed transitions $^4A_2 \rightarrow {}^4T_1$ ($^4$F) and $^4A_2 \rightarrow {}^4T_2$ ($^4$F) occur at about 7000 and 4000 cm$^{-1}$, respectively [35–37]. The only spin-allowed transition in the visible region is $^4A_2 \rightarrow {}^4T_1$ ($^4$P), which dominates the spectrum of the considered crystal. It is easily observed as a wide structured band centered at around 15,000 cm$^{-1}$. All other narrow bands are due to the spin-forbidden transition to the spin-doublet states. The experimental absorption spectrum of TMA-CoC measured by means of the Shimadzu 160A double beam automatic scanning spectrophotometers is shown in Fig. 2 (solid line). The IR region, in which both $^4A_2 \rightarrow {}^4T_2$ ($^4$F) and $^4A_2 \rightarrow {}^4T_1$ ($^4$F) transitions lie, was outside the spectrometer range.

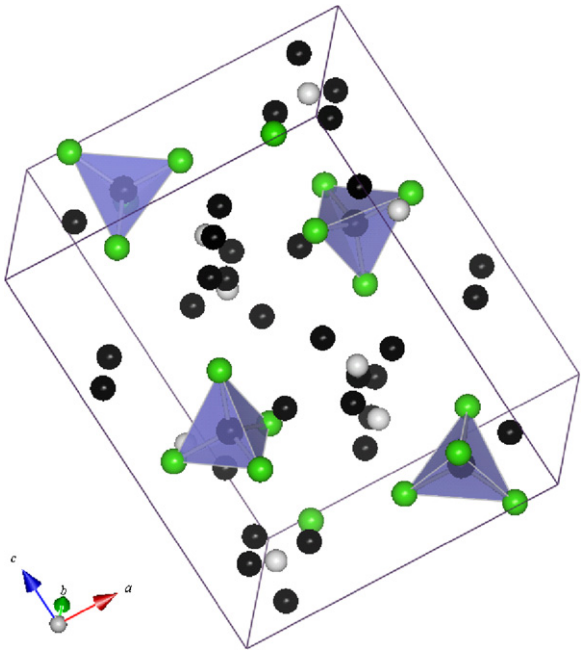


Fig. 1. One unit cell of $(N(CH_3)_4)_2CoCl_4$. $Co^{2+}$ ions are at the centers of chlorine tetrahedral. Carbon and nitrogen atoms are in black and white colors, respectively. Positions of hydrogen atoms were not detected in Ref. [33]. Drawn with VENUS developed by Izumi and Dilanian.

5*d*-electrons of $Mn^{2+}$ produce 16 LS terms ($^6$S, $^4$PDFG, $^2$SPD$_1$D$_2$D$_3$F$_1$F$_2$G$_1$G$_2$HI), these terms in a crystal field create 100 energy levels (without additional spin-orbit splitting). The

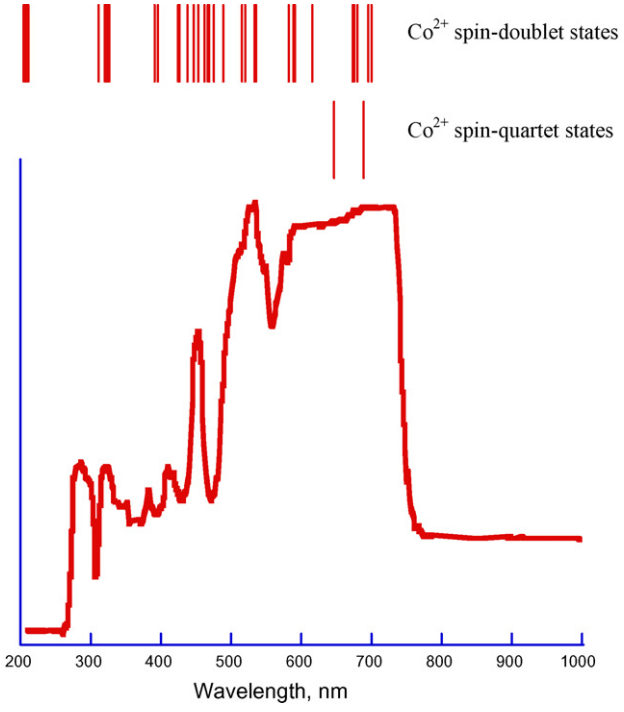


Fig. 2. Absorption spectrum of $[N(CH_3)_4]_2CoCl_4$ crystal. Calculated $Co^{2+}$ energy levels are shown by vertical lines at the top of figure (see text for details).