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Pressure dependence of the crystal field spectrum of the NH_4MnCl_3 perovskite: correlation between 10Dq, Ne and Nt, and the Mn–Cl distance in $MnCl_6^{4-}$ complexes

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Abstract

This work investigates the pressure-dependence of the crystal field (CF) spectrum of $MnCl_6^{4-}$ complexes in NH_4MnCl_3. The aim is to determine the variation of 10Dq as well as the bonding parameters Ne and Nt deduced from the absorption spectra, with the Mn–Cl distance. The selected crystal provides a perfect O_h symmetry for Mn^{2+} allowing a direct correlation between the pressure and the Mn–Cl distance through the bulk modulus. Precise values of the variations of the spectroscopic parameters with P were obtained from the linear behaviour exhibited by the six single CF excitations in the 0–60 kbar range. It is worth pointing out that an R-dependence of 10Dq on the basis of a KR^{-n} variation with n close to 7 was attained from the pressure-induced shifts. A remarkable feature is the reduction of Ne and Nt upon pressure. Although Ne < Nt due to the greater bonding character of the e_g-orbitals, its variation with pressure however is smaller than that of the π-bonding t_{2g}-related Nt parameter. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The knowledge of how electronic spectra of transition metal (TM) complexes depend on bond distances is relevant for a microscopic understanding of the processes involved in the optical phenomena as well as for attaining a proper description of the electronic structure when a given TM complex is formed in different crystal lattices. In particular, the study of the crystal field (CF) spectrum of octahedral (O_h) MX_6^{4-} complexes and its dependence on the M–X distance, R, provides a direct correlation between the electronic structure of the 3d-valence electrons, strongly dependent on the covalent character of the M–X bond, and R. The interest to establish structural correlations in these systems is twofold. Firstly, we can obtain direct information about the R-dependence of the CF parameter, 10Dq, representing the splitting of the

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mainly TM e_g and t_{2g} orbitals, as well as on the corresponding Ne and Nt bonding parameters, related to the molecular orbital (MO) wavefunction as [1–4]

$$|e_g\rangle = \mathrm{Ne}\ (|d_{3z2-r2,x2-y2}\rangle - \lambda_e|L_e\rangle),$$

$$|t_{2g}\rangle = \mathrm{Nt}\ (|d_{xy,yz,xz}\rangle - \lambda_t|L_t\rangle), \quad (1)$$

where d and L represent the TM d-orbitals and the symmetry-adapted linear combinations of the ligand p- and s-orbitals, respectively. We notice that, stronger the mixing of metal and ligand functions smaller is the corresponding *N*. Secondly, this correlation is noteworthy as an alternative method to the EXAFS technique for deriving precise M–X distances from the optical spectra of TM impurities [5]. Although this procedure has already been used for R estimates in MnF_6^{4-} and $MnCl_6^{4-}$ impurities formed in perovskites $ABX_3 : Mn^{2+}$ (X = F, Cl) on the basis of a $10Dq = KR^{-5}$ law [5–7], this variation of 10Dq (*R*) has not yet been obtained experimentally from pure Mn^{2+} systems. First pressure measurements on $MnCl_2$ [8] were not adequate for such purpose due to the low crystal symmetry.

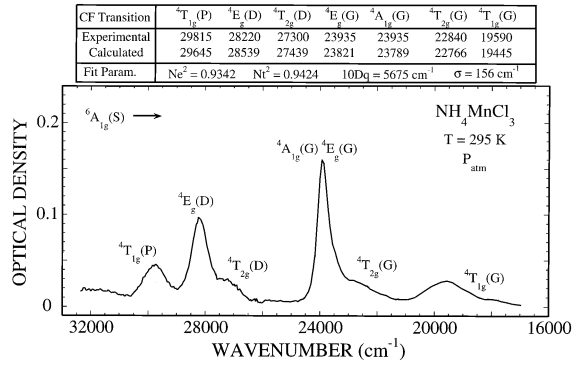
This work investigates the pressure-dependence of the CF spectrum of $MnCl_6^{4-}$ complexes in the NH_4MnCl_3 perovskite. The aim is to determine the variation of the CF splitting 10Dq as well as Ne and Nt for Mn^{2+} deduced from the optical absorption (OA) spectra [9], with the actual Mn–Cl distance. The use of NH_4MnCl_3 (*Pm3m* space group) is advantageous since it gives a perfect O_h environment for Mn^{2+} [10]. Furthermore, the election of Mn^{2+} for such a study is due to the rich multiplet structure arising from the d^5 configuration. The six CF bands usually observed in the OA spectrum provide not only suitable values of 10Dq but also of the Ne and Nt (Koide–Price formalism [1,2]) or the *B* and *C* Racah parameters (Tanabe–Sugano model [11]), in contrast to other TM ions where apart from 10Dq, the Ne and Nt values may be difficult to determine [9,12].

2. Experimental

Single crystals of NH_4MnCl_3 were grown by the Bridgman technique from the melt at 481°C. The *Pm3m* cubic symmetry was checked by X-ray diffraction and by means of a polarizing microscope. The OA spectra under pressure were obtained by means of an implemented single beam microspectrometer [13] using a UV fused silica optical-fiber bundle (Ø = 1 mm). This procedure improved the signal-to-noise ratio by an order of magnitude thus enabling to measure OA bands with optical densities smaller than 0.02. The pressure was applied with a DAC (High Pressure Diamond Optics, Inc) and calibrated from the Ruby R-line shift.

3. Optical absorption spectra of NH_4MnCl_3: pressure-dependence

Fig. 1 shows the OA spectrum of NH_4MnCl_3 obtained at atmospheric pressure. Both the peak energy and the spectrum shape are characteristic of Mn^{2+} CF transitions (d–d) within $MnCl_6^{4-}$ [10]. In fact, the OA spectrum is very similar to the excitation spectra obtained from isolated $MnCl_6^{4-}$ complexes formed along the $ABCl_3 : Mn^{2+}$ chloroperovskite series [6]. The slight variations of peak energy observed along the series followed the



CF Transition	$^4T_{1g}$(P)	^4E_g(D)	$^4T_{2g}$(D)	^4E_g(G)	$^4A_{1g}$(G)	$^4T_{2g}$(G)	$^4T_{1g}$(G)
Experimental	29815	28220	27300	23935	23935	22840	19590
Calculated	29645	28539	27439	23821	23789	22766	19445
Fit Param.	$Ne^2 = 0.9342$	$Nt^2 = 0.9424$	10Dq = 5675 cm^{-1}	$\sigma = 156$ cm^{-1}			

Fig. 1. Absorption spectrum of NH_4MnCl_3 at $T = 295$ K and atmospheric pressure. Crystal dimensions: $100 \times 100 \times 30\ \mu m^3$. The bands are identified by the commonly used labels. The calculated energies represent the least-squares fit to the d^5-multiplet energy as a function of 10Dq, Nt^2, Ne^2. Units are in cm^{-1}. Within the Tanabe–Sugano model: $B = 742$, $C = 3042$, $10Dq = 5660$ and $\sigma = 160\ cm^{-1}$. The Trees and Seniority corrections were considered in both models using fixed values of $\alpha = 67$ and $\beta = -131\ cm^{-1}$, respectively [5].

trends of the Tanabe–Sugano diagram on the basis of 10Dq changes induced by chemical pressure effects [6,7]. The six bands of Fig. 1 correspond to CF transitions of the $MnCl_6^{4-}$ complex and are identified with the commonly used labels. The experimental CF energies at atmospheric pressure are given in Fig. 1 together with the calculated ones obtained by least-square fitting. The d^5 energy matrices as a function of 10Dq, Ne and Nt (or the corresponding B and C Racah parameters) are given elsewhere [2,9]. The Trees (α) and Seniority (β) corrections were introduced through the appropriated matrices [5]. Note that the reduction of Ne and Nt (or B and C) with respect to the 'free ion' values, Ne = 1 and Nt = 1 ($B_0 = 918$ and $C_0 = 3273\ cm^{-1}$) [2] is just a bonding effect, i.e. the electronic wavefunction within the complex is no longer a pure Mn^{2+} orbital but a MO as expressed in Eq. (1). In NH_4MnCl_3, the Mn–Cl distance, R, is related to the lattice parameter by $R = a/2$, and therefore the cell volume reduction upon hydrostatic pressure can be easily connected with P through the bulk modulus as $\Delta P = -3B(P)\ \Delta R/R$.

The variation of the OA spectrum with pressure is shown in Fig. 2. As regards the pressure-induced shifts two important facts must be underlined. (i) The strongly 10Dq-dependent $^4T_{1g}$ and $^4T_{2g}$ (G) bands shift to lower energy at rates of -37 and $-28\ cm^{-1}$/kbar, respectively. Given that the corresponding electronic transitions chiefly involve interconfigurational changes from $t_{2g}^3e_g^2$ to $t_{2g}^4e_g^1$ ($E[^4T_{1g}(G)] \propto -10Dq$) [11], these red-shifts clearly reflect an increase of 10Dq upon pressure, as expected by the CF increase induced by decreasing R. On the other hand, the narrow 10 Dq-independent $^4A_{1g}$,^4E_g(G) peak within the $t_{2g}^3e_g^2$ configuration also experiences a red-shift upon pressure ($\partial E/\partial P = -9\ cm^{-1}$/kbar), but four times smaller than the $^4T_{1g}$ (G) shift. This result is noteworthy since this shift, $\Delta E = 10\ \Delta B + 5\ \Delta C$, is directly associated with a reduction of the Racah parameters (or Ne and Nt) with P. (ii) The six CF energies vary linearly with pressure in the investigated 0–60 kbar range. This behaviour allows us to establish an easy correlation between the spectroscopic parameters and R, through the atmospheric-pressure bulk modulus, $B(0)$.

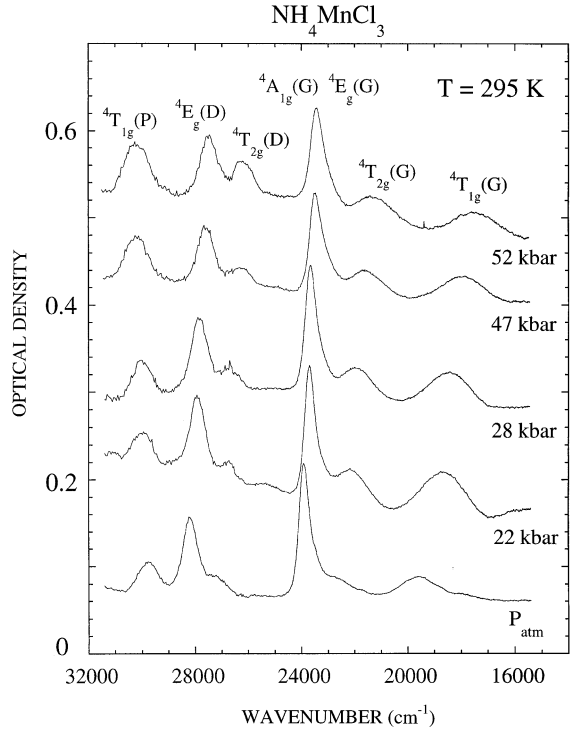


Fig. 2. Variation of the optical absorption spectrum of NH_4MnCl_3 with pressure. Crystal dimensions: $100 \times 100 \times 30\ \mu m^3$.

4. Variation of 10Dq, Ne and Nt with the Mn-Cl distance, *R*

The variation of the spectroscopic parameters obtained through the experimental CF energies, $E_i(P)$, $i = 1, \ldots, 6$, with pressure is shown in Fig. 3. From the linear pressure-dependence shown by 10Dq ($\partial 10Dq/\partial P = +28\ cm^{-1}$/kbar), we can derive for the first time the R-dependence of 10Dq for $MnCl_6^{4-}$. The partial derivatives of 10Dq with respect to P and R at atmospheric pressure are related by the following equation:

$$(\partial 10Dq/\partial R)_{R=R_0} = (\partial 10Dq/\partial P)_{P_0}/(\partial R/\partial P)_{P_0}$$

$$\text{with } (\partial R/\partial P)_{P_0} = -R_0/[3\ B(0)]. \quad (2)$$

Assuming that $10Dq = KR^{-n}$ and taking $R_o = 2.525(4)$ Å [10], $B(0) = 500(50)$ kbar [14] and

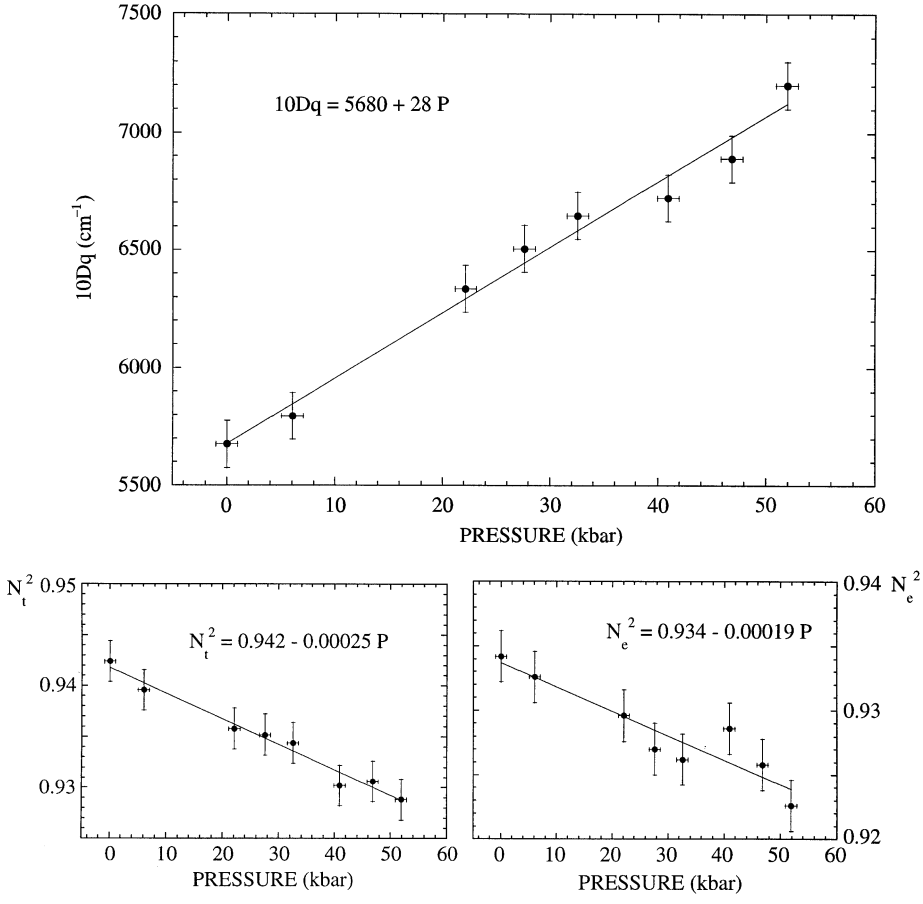


Fig. 3. Variation of the spectroscopic parameters 10Dq, Nt^2 and Ne^2 with pressure.

$10Dq_0 = 5675\ (100)\,cm^{-1}$ (Fig. 1), we obtain $(\partial R/\partial P)_{P_0} = -1.7\times10^{-3}$ Å/kbar, and an exponent n,

$$n = (R_0/10Dq_0)(\partial 10Dq/\partial R)_{R=R_0} = (3B(0)/10Dq_0)(\partial 10Dq/\partial P)_{P=P_0} = 7.4(1). \quad (3)$$

At variance with what is measured for Mn^{2+} in fluorides [5] or NiO [15], the value of n is in the present case clearly higher than $n = 5$ obtained in the point charge model. It is worth noting however that crystal-field theory predicts 10Dq values which are much smaller than the experimental ones [5]. MO calculation on different TM complexes lead to n values in the 3.5–6.5 range as well as to reasonable 10Dq values [4]. The strong sensitivity of 10Dq to R variations whose origin is analysed elsewhere [16], can be used for detecting changes of the metal–ligand distance through shifts of the $^4T_{1g}(G)$ band. This procedure is particularly useful for Mn-doped materials since it provides a distance sensitivity $\Delta R = [(\partial R/\partial P)_{P_0}/(\partial E/\partial P)_{P_0}]\Delta E \sim 0.003$ Å for a $^4T_{1g}(G)$ shift of $\Delta E \sim -60\,cm^{-1}$, thus improving by an order of magnitude the current EXAFS sensitivity ($\Delta R \sim 0.01$ Å) [7].

The obtained Ne^2 and Nt^2 values confirm the high ionicity of the $MnCl_6^{4-}$ units. As for the relative reduction of Ne^2 and Nt^2 upon P (Fig. 3) let us write $n_i = -\partial \mathrm{Ln}\, Ni^2/\partial \mathrm{Ln}\, R$ (i = e, t). The values $n_t = -0.4$ and $n_e = -0.3$ derived experimentally stress that covalent coefficients Ni^2 are only slightly dependent on R. This is in qualitative agreement with the results of MO calculations on

MnF_6^{4-} [16] and underlines that $Ni\lambda_i$ coefficients depend not only on the overlap between metal and ligand wavefunctions but also on the separation between mainly 3d(Mn) and 3p(Cl) levels [17]. That separation increases significantly when R decreases. As B depends on Ne^4, Nt^4 and Ne^2Nt^2 [2], the present results indicate that for $MnCl_6^{4-}$, B is much less sensitive to R than 10Dq [6]. Similar results were obtained for Mn^{2+}-doped ZnS [18].

The fact that $|\partial Nt^2/\partial P| > |\partial Ne^2/\partial P|$ could reflect that π overlap integrals, S_t, are more sensitive to R than the σ ones, S_e. Indeed roughly assuming that λ_i is proportional to S_i, then Ni^2 can be approached by $1-\alpha S_i^2$ and therefore we can justify not only why $Nt > Ne$ but also that $|\partial Nt^2/\partial P| > |\partial Ne^2/\partial P|$ in terms of the respective overlap integrals and their variation with R. Work along this line is in progress.

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References

[1] S. Koide, M.H.L. Pryce, Philos. Mag. 3 (1958) 607.
[2] D. Curie et al., J. Chem. Phys. 61 (1958) 3048.
[3] M. Flórez et al., Phys. Rev. B 34 (1986) 1200.
[4] M. Moreno et al., J. Phys.: Condens. Matter 4 (1992) 9481.
[5] F. Rodríguez, M. Moreno, J. Chem. Phys. 84 (1986) 692.
[6] M.C.M. de Lucas et al., J. Lumin. 60/61 (1994) 581.
[7] M.C.M. de Lucas et al., J. Phys. Chem. Sol. 56 (1995) 995.
[8] J.C. Zahner, H.G. Drickamer, J. Chem. Phys. 35 (1961) 1483.
[9] J.S. Griffith, in: The theory of Transition-Metal Ions, Cambridge University Press, Cambridge, 1980.
[10] F. Agullo-Rueda et al., Solid State Commun. 60 (1986) 331.
[11] Y. Tanabe, S. Sugano, J. Phys. Soc. Japan 9 (1954) 753.
[12] A.B.P. Lever, in: Inorganic Electronic Spectroscopy Studies in Physical and Theoretical Chemistry, Elsevier, New York, 1984.
[13] B.A. Moral, F. Rodríguez, Rev. Sci. Instrum. 66 (1995) 5178.
[14] C. Pique et al., Ferroelectrics 109 (1990) 27.
[15] H.G. Drickamer, C.W. Frank, in: Electronic Transitions and the High Pressure Chemistry and Physics of Solids, Chapman & Hall, London, 1973.
[16] M. Moreno et al., Int. J. Quantum Chem. 52 (1994) 829.
[17] J. Aramburu et al., J. Phys.: Condens. Matter 4 (1992) 9089.
[18] K. Mayrhofer et al., J. Phys. C 21 (1988) 4393.