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Double-excitation transitions in the perovskite NH_4MnCl_3 studied by pressure techniques

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This work investigates double-excitation (DE) transitions in the cubic chloroperovskite NH_4MnCl_3 through high-pressure absorption spectroscopy. This procedure has proved to be a powerful tool for revealing DE from the peak energy variations induced by pressure. Particularly, this is important for manganese chlorides where DE assignment is a difficult task to accomplish given that the associated bands appear in the absorption threshold and overlap with several Mn^{2+} single excitation (SE) bands. Apart from Mn^{2+} SE, the optical-absorption spectrum of NH_4MnCl_3 microcrystals shows a new intense band at 39 200 cm^{-1} that is assigned to the ${}^4T_{1g}+{}^4T_{1g}$ DE transition. The proposed assignment is based on the transition energy as a sum of the corresponding SE energies, $E({}^4T_{1g}+{}^4T_{1g})=E({}^4T_{1g})+E({}^4T_{1g})$, and is clearly confirmed by the variation of the band position with pressure. The measured pressure shift of $\partial E/\partial P=-76\ \mathrm{cm}^{-1}/\mathrm{kbar}$ is twice the pressure shift experienced by the first ${}^4T_{1g}(G)$ SE located at 19 590 cm^{-1}, $\partial E/\partial P=-37\ \mathrm{cm}^{-1}/\mathrm{kbar}$. From this result, the possibility of SE transitions ${}^4A_{2g}(F)$, ${}^4T_{1g}(F)$, and ${}^4T_{2g}(F)$ located around 40 000 cm^{-1} as responsible for this band is definitively ruled out due to their different pressure shift. [S0163-1829(99)10939-1]

I. INTRODUCTION

The presence of double excitation (DE) bands in the electronic spectra of transition-metal compounds is a rather unusual phenomenon that, in contrast to single excitations (SE), cannot be explained on the basis of the MX_6 (M: transition ion; X: ligand) molecular complex. A DE is an electronic transition involving excited pair states and therefore can only occur in exchanged-coupled systems.[1–5] The interest in researching DE phenomena is twofold. Firstly, they attract interest because a DE provides a direct way of simultaneously exciting two metal ions with one single photon. Secondly, DE can be used as probes to detect aggregated phases in insulating materials through nondestructive techniques like optical spectroscopy. This latter aspect was exploited to identify precipitates in Mn^{2+} -doped alkali halides.[6–8]

The effective spin-dependent mechanism governing the transition intensity in exchange coupled systems was first proposed, to our knowledge, by Tanabe[9] to explain the optical spectra of Mn-Mn dimers The effective transition moment is given by

$$\mathbf{D}_{\mathrm{eff}}=\sum_{i,j}\left(\prod{}_{A_iB_j}\right)\cdot\mathbf{s}_{A_i}\cdot\mathbf{s}_{B_j}; \qquad (1)$$

the α component ($\alpha=x,y,z$) of the $\Pi_{A_iB_j}$ vector as a function of the orbital exchange parameters is given by

$$\prod_{A_iB_j}^{\alpha}=\left(\frac{\partial J_{A_iB_j}}{\partial E^{\alpha}}\right)_{E\to 0},$$

where $J_{A_iB_j}$ is an exchange coupling element between the two excited states, $\mathbf{E}$ is the radiation electric field, and i and j number the singly occupied orbitals on the ions A and B.

This mechanism explains the different temperature dependence of the SE and DE intensities $I(T)$ in pure Mn^{2+} compounds such as $RbMnF_3$,[1–3,10,11] MnF_2,[2,3,10] $KMnF_3$[2,11] and $BaMnF_4$.[12] This distinct thermal behavior exhibited by the exchange-induced DE transitions ${}^6A_{1g}{}^A(S)+{}^6A_{1g}{}^B(S)\to{}^4\Gamma_i{}^A+{}^4\Gamma_j{}^B$ and SE transitions ${}^6A_{1g}{}^A(S)+{}^6A_{1g}{}^B(S)\to{}^6A_{1g}{}^A(S)+{}^4\Gamma_g{}^B$, together with the DE transition energy as sum of the corresponding single excitations: $E[{}^4\Gamma_i+{}^4\Gamma_j]\approx E[{}^4\Gamma_i]+E[{}^4\Gamma_j]$, have been the basis for DE assignment in these manganese fluoride model systems.

In this work we investigate DE transitions in the cubic chloroperovskite NH_4MnCl_3 through high-pressure absorption spectroscopy. This new procedure has proved to be a powerful tool for revealing DE through the band-energy variations induced by pressure. In particular, this has special interest for manganese chlorides where DE assignment is a difficult task to accomplish, given that, in contrast to fluorides, DE bands appear near the absorption threshold and overlap with several Mn^{2+} single excitation (SE) bands. The pioneering work of Gosh and Mukherjee on Rb_2MnCl_4 is an example of this behavior.[13] The absorption threshold in chlorides is associated with the tail of the intense $Cl^-\to Mn^{2+}$ charge-transfer band ($f=0.14$) whose maximum is placed about 58 000 cm^{-1}.[14] In fluorides, however, the corresponding $F^-\to Mn^{2+}$ charge-transfer energy is shifted 27 000 cm^{-1} to higher energies with respect to chlorides,[15] thus providing a large spectral region to investigate DE transitions. We select NH_4MnCl_3 ($Pm3m$; $a=5.050$ Å) (Ref. 16) because it is, together with $TlMnCl_3$, the only manganese trichloride with the perovskite structure at ambient conditions.[17] The crystal becomes antiferromagnetic below $T_N=105$ K. Its structure provides a perfect octahedral symmetry for Mn^{2+} making it attractive for structural correlation studies. Throughout this research, we show the usefulness of pressure techniques to identify DE from the variation of the absorption bands under

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pressure. In particular, a new intense band observed at 39 200 cm^{-1} in NH_4MnCl_3 has been assigned to the first $^4T_{1g}(G)+{}^4T_{1g}(G)$ DE transition. This band can be clearly distinguished from other overlapping Mn^{2+} SE bands such as $^4A_{2g}(F)$, $^4T_{1g}(F)$, and $^4T_{2g}(F)$, by their different pressure shift.[18] Its assignment to a DE is based on the pressure redshift of $\partial E/\partial P = -76\,\mathrm{cm}^{-1}$/kbar in comparison to the pressure redshift of $\partial E/\partial P = -37\,\mathrm{cm}^{-1}$/kbar undergone by the first $^4T_{1g}(G)$ band at 19 590 cm^{-1}.

II. EXPERIMENT

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 the optical quality by means of a polarizing microscope. The optical-absorption (OA) spectra under pressure were obtained by means of a single beam microspectrometer especially designed for use with diamond-anvil cells (DAC).[19,20] The light coming from either a deuterium or a tungsten lamp is focused by an Ealing reflective objective into a 30-μm spot in the hydrostatic cavity. The transmitted light is collected through an uv fused silica optical-fiber bundle ($\varnothing = 1$ mm) attached to a HR320 Jobin-Yvon monochromator. This procedure improved the signal-to-noise ratio by an order of magnitude with respect to a previously used standard setup,[20] thus enabling to measure OA bands with optical densities ranging from about 0.01 to 5. The upper limit is significantly reduced below 300 nm due to the diamond absorption. A parallelepiped single crystal of $100\times100\times30\,\mu\mathrm{m}^3$ was used in the pressure experiments. The pressure was applied with a DAC (High Pressure Diamond Optics, Inc) and calibrated through the R-line shift of a Ruby chip placed near the NH_4MnCl_3 crystal inside the cavity. A Merck spectroscopic paraffin oil was employed as a pressure transmitter in order to avoid moisture. The Ruby luminescence was excited with the 568 nm line of a I-302-K Coherent Krypton laser using the experimental setup described elsewhere.[19,20]

The OA spectra at ambient pressure of massive crystals of $3\times3\times0.5\,\mathrm{mm}^3$ were obtained on a Lambda 9 Perkin-Elmer spectrophotometer. Band analysis was performed using suitable spectroscopic software.

III. RESULTS AND DISCUSSION

Figure 1 compares the OA spectra of NH_4MnCl_3 at atmospheric pressure obtained from single crystals of 0.5 mm thickness and microcrystals. The spectrum [1(a)] was taken with a conventional spectrophotometer and is very similar to that reported previously.[21] Bands correspond to Mn^{2+} SE from the $^6A_{1g}(S)$ ground state to different spin quartet excited states $^4\Gamma_g$ as indicated in Fig. 1. The analysis of the transition energies provides values of the Racah parameters ($B=742\,\mathrm{cm}^{-1}$ and $C=3042\,\mathrm{cm}^{-1}$) and the ligand field parameter ($10\,\mathrm{Dq}=5660\,\mathrm{cm}^{-1}$) characteristic of octahedral $MnCl_6^{4-}$ complexes[17] according to the perovskite structure of the NH_4MnCl_3 crystal.[16] Interestingly, the use of NH_4MnCl_3 microcrystals [Fig. 1(b)] enables us to explore into the absorption threshold in the uv region. The presence of a new intense band at 39 200 cm^{-1} is noteworthy. Its oscillator strength is an order of magnitude higher than those of SE transitions, and the corresponding energy is just twice the energy of the first $^4T_{1g}(G)$ SE band ($E=19\,590\,\mathrm{cm}^{-1}$) at $P=0$. Analogous to Rb_2MnCl_4,[13] the present result suggests that this band most likely corresponds to the $^6A_{1g}{}^A(S) + {}^6A_{1g}{}^B(S) \rightarrow {}^4T_{1g}{}^A(G) + {}^4T_{1g}{}^B(G)$ DE transition. However, a DE assignment based only on the transition energy must be taken with caution given that the energy of the first DE $^4T_{1g}^A(G)+{}^4T_{1g}^B(G)$ and the highest energy SE $^4T_{1g}(F)$, $^4T_{2g}(F)$ and $^4A_{2g}(F)$ are very similar. The calculated energies from the B, C, and 10 Dq values derived by fitting from the first six SE bands are $40\,460\,\mathrm{cm}^{-1}\,[^4T_{1g}(F)]$, $38\,650\,\mathrm{cm}^{-1}\,[^4T_{2g}(F)]$, and $38\,150\,\mathrm{cm}^{-1}\,[^4A_{2g}(F)]$ at $P=0$ kbar. From these estimates, we tentatively assign the small shoulder observed in the optical spectrum at about 37 000 cm^{-1} to the Mn^{2+} $^4A_{2g}(F)$ SE.[20]

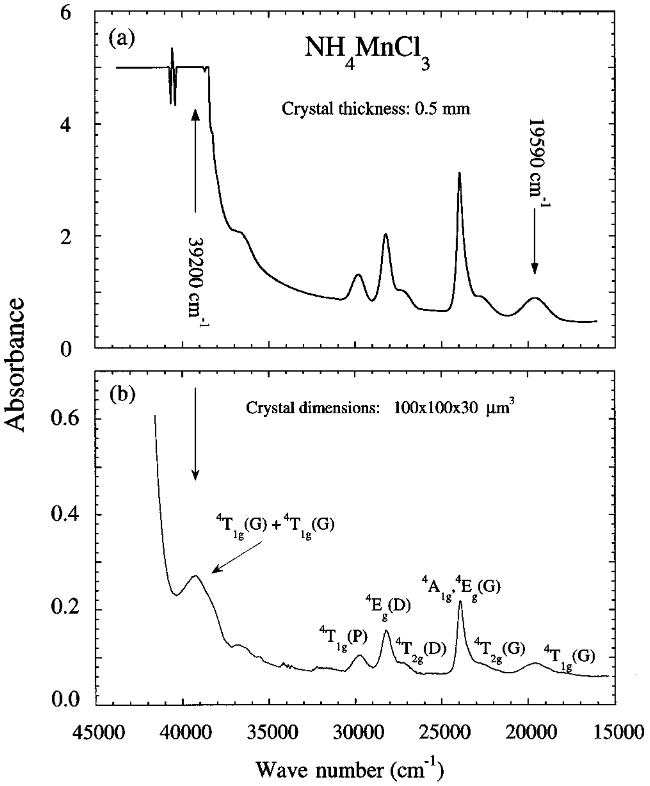

FIG. 1. (a) Optical-absorption spectrum of the NH_4MnCl_3 perovskite at ambient pressure and room temperature recorded with a conventional spectrometer. Crystal dimensions: $3\times3\times0.5\,\mathrm{mm}^3$. The horizontal line in the uv region indicates the detection limit of the instrument. (b) Optical-absorption spectrum of a NH_4MnCl_3 microcrystal ($100\times100\times30\,\mu\mathrm{m}^3$) obtained with the experimental setup described elsewhere (Refs. 19 and 20). Bands are identified with the commonly used labels (Refs. 17 and 21). Although the energy of the Mn^{2+} single excitation bands are the same in (a) and (b), note the presence of an intense band at 39 200 cm^{-1} in (b).

The variation of the OA spectrum with hydrostatic pressure clearly reveals the origin of the 39 200 cm^{-1} band through its pressure shift. According to the Tanabe-Sugano diagram for d^5 ions,[18] the three $^6A_{1g}(S)\rightarrow{}^4\Gamma_g(F)$ SE of highest energy and the first DE exhibit different 10 Dq dependences. While transitions $^6A_{1g}(S)\rightarrow{}^4T_{1g}(F)$ and $^4T_{2g}(F)$ are mainly associated with change of electronic configuration from $t_{2g}^3e_g^2$ to $t_{2g}^2e_g^3$, and are thus proportional to +10 Dq, the $^6A_{1g}(S)\rightarrow{}^4A_{2g}(F)$ is 10 Dq independent.

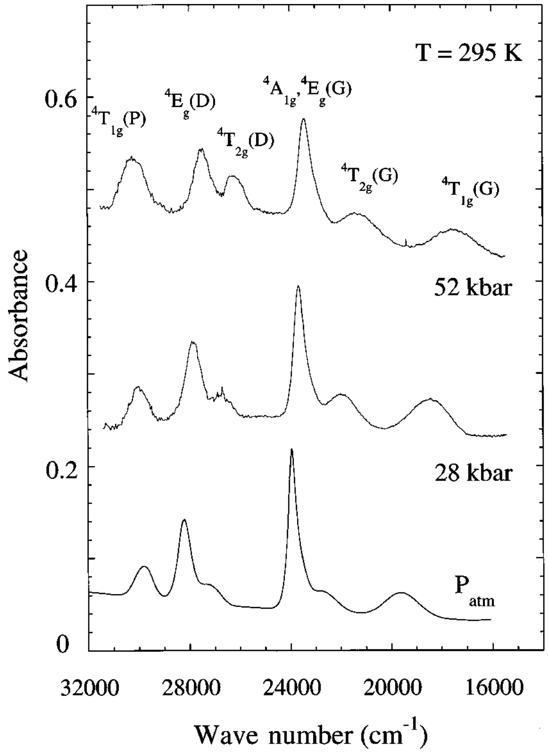

FIG. 2. Variation of the optical-absorption spectrum of the NH_4MnCl_3 microcrystal with pressure at $T=295$ K. Note the different shifts undergone by the $^4T_{1g}(G)$ and $^4A_{1g}{}^4E_g(G)$ bands. The spectra are displaced for comparison purposes.

Therefore, the first DE transition energy, $E[^4T_{1g}{}^A(G)+^4T_{1g}{}^B(G)]\approx E[^4T_{1g}{}^A(G)]+E[^4T_{1g}{}^B(G)]$, should be proportional to -20 Dq, given that the first $^4T_{1g}(G)$ excited state mainly corresponds to the $t_{2g}^4e_g^1$ configuration. Consequently, an increase of 10 Dq upon pressure induced by a reduction of the Mn-Cl distance (cell volume contraction), must lead to an important DE redshift, in contrast to the relatively smaller blueshift undergone by the SE $^4T_{1g}(F)$ and $^4T_{2g}(F)$, and even smaller by $^4A_{2g}(F)$.

Figures 2 and 3 show the variation of the OA spectrum of NH_4MnCl_3 with pressure in the 0–60 kbar range. The variation of the six SE bands under pressure follows the trends of the Tanabe-Sugano diagram for an increase of 10 Dq and a decrease of B and C. It is worth noting that the redshift experienced by the first $^4T_{1g}(G)$ and $^4T_{2g}(G)$ bands under pressure reflects the increase of 10 Dq expected for transitions involving changes of electronic configuration from the $t_{2g}^3e_g^2$ ground state to the $t_{2g}^4e_g^1$ excited configuration.[18] The intense uv band at 39 200 cm^{-1} experiences an enormous redshift of 4000 cm^{-1} from 0 to 60 kbar. The corresponding shift rate of $\partial E/\partial P=-76\,cm^{-1}$/kbar is just twice the $^4T_{1g}(G)$ rate as is shown in Fig. 4. This feature strongly supports the assignment of this band to the $^4T_{1g}{}^A(G)+^4T_{1g}{}^B(G)$ DE transition. It must be noted that in this assignment we are assuming that the DE energy can be expressed as the sum of the SE energies. The goodness of this approximation depends on the magnitude of the two-exciton stabilization energy with respect to the sum of SE energies. In NH_4MnCl_3, this is smaller than the peak-energy accuracy and the approximation is valid. Although the main features of the spectra of Fig. 3 have been explained on the basis of a DE band, note that this band seems to present a double peaked structure upon increasing pressure. However, we are not able to distinguish whether the observed structure is associated with a real DE splitting, or is due to the scattering of data produced by the lower resolution of the instrument at high pressure.

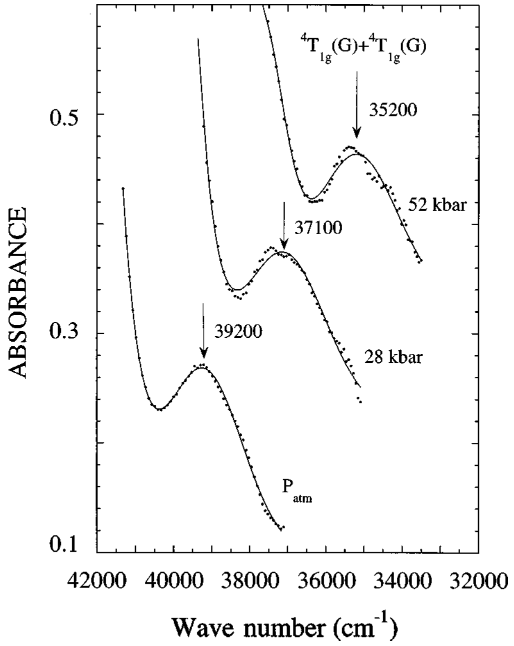

FIG. 3. Variation of the uv band at 39 200 cm^{-1} in NH_4MnCl_3 with pressure at room temperature. The spectra have been fitted to the sum of an absorption background plus a single Gaussian which are shown (full lines) together with the absorption data (points). Arrows indicate the maximum position of the fitted Gaussian band. Note the important redshift experienced by this band (-76 cm^1/kbar) in comparison to the single excitation shifts shown in Fig. 2. The spectra are displaced for comparison purposes.

The comparison of the measured pressure shifts for DE and SE provides an useful estimate of the energy difference, $\Delta E=E(^4T_{1g}^A+^4T_{1g}^B)-2E(^4T_{1g})$, over a wide pressure range. Indeed it indicates that the DE energy deviates about 5% the sum of the involved SE energies. From this estimate

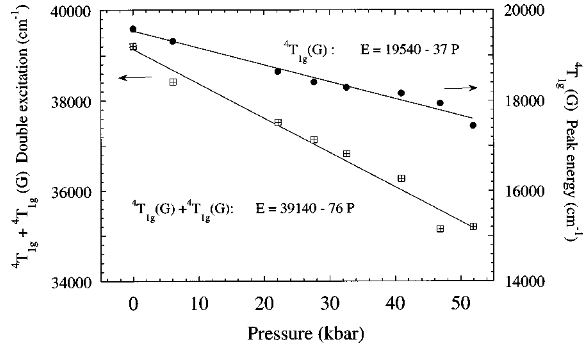

FIG. 4. Variation of the peak energy of the uv band at 39 200 cm^{-1} and the first $^4T_{1g}$ band at 19 590 cm^{-1} with pressure in the 0–60 kbar range. Straight lines represent the least-square linear fits of the experimental data. Note that the shift rate of the uv band is almost exactly twice the shift rate of the $^4T_{1g}(G)$ single excitation band.

we conclude that a DE assignment based exclusively on the transition energy must be taken with caution.

It is worth pointing out that the present procedure of assigning DE based on the pressure shifts, cannot be analogously applied to the thermal shifts. While the expected pressure shift for a given ${}^4\Gamma_i^A + {}^4\Gamma_i^B$ DE is twice the corresponding ${}^4\Gamma_i$ SE pressure shift, this is not the case for the corresponding thermal shift $\delta_T({}^4\Gamma_i^A + {}^4\Gamma_i^B) \neq 2\,\delta_T({}^4\Gamma_i)$, due to the explicit contribution $[\delta E/\delta T]_v$.[22,23] Thermal shifts at constant pressure can be expressed in terms of the energy derivatives with respect to the temperature as given in Eq. (2):

$$[\partial E/\partial T]_p = [\partial E/\partial V]_T [\partial V/\partial T]_P + [\partial E/\partial T]_v . \tag{2}$$

The first term on the right-hand side, named the implicit contribution, represents the thermal shift associated with changes of volume by thermal expansion effects, whereas the second term named explicit contribution accounts for the shift induced by changes of temperature at constant volume. A detailed analysis of the different thermal shift contributions in MnF_6^{4-} systems is given elsewhere.[23] The implicit contribution to the DE thermal shift should be twice the SE shift like in pressure experiments. But the explicit contribution strongly depends on the difference between ground-state and excited state vibrational frequencies,[22,23] and therefore can be similar for DE and the corresponding SE transitions. In $KMnF_3$ and $RbMnF_3$,[22] the measured implicit contribution represents 40% of the total thermal shift, thus δ_T(DE) is not necessarily the sum of the corresponding SE thermal shifts δ_T(SE). The comparison of the thermal shifts undergone by the DE bands ${}^4T_{1g} + {}^4T_{1g}(\alpha)$, ${}^4T_{1g} + {}^4T_{2g}(\beta)$, and ${}^4T_{1g} + {}^4A_{1g}{}^4E_g(\delta)$ DE in MnF_2, $KMnF_3$, $RbMnF_3$[10,11] and $BaMnF_4$ (Ref. 12) in the 10–300 K temperature range, and the variations of the respective SE confirms this behavior, stressing the inadequacy of thermal shifts for assigning DE.

IV. CONCLUSIONS

We have shown that high-pressure optical spectroscopy is a suitable tool to identify double excitation bands in the OA spectrum of transition-metal compounds. In particular, the new uv band at 39 200 cm^{-1} observed in NH_4MnCl_3 has been assigned to the ${}^4T_{1g}(G) + {}^4T_{1g}(G)$ double excitation through its pressure-induced redshift. Furthermore the pressure technique allows us to distinguish DE from SE of the same energy in manganese compounds by their different pressure shift. The comparison of the pressure shift rates of DE and SE provides a direct way of assigning DE in terms of the parent SE transitions.

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