

4 December 2000

PHYSICS LETTERS A

Physics Letters A 277 (2000) 281–286

www.elsevier.nl/locate/pla

## Excitonic two-phonon progressions in transition metal compounds

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Received 23 July 2000; accepted 19 October 2000 Communicated by J. Flouquet

## Abstract

Evidence of two-phonon structures is reported for some intra-configurational crystal field transitions in layered V- and Crhalides. In particular, the crystal field spectrum of  $CrBr_2$  (3d<sup>4</sup>) has been shown for the first time, since the exciton–phonon interaction, despite its unfilled  $e_g$  orbitals, vanishes to first order yielding a two-phonon sequence in the  ${}^{3}A_{1}(G) + {}^{3}A_{2}(F)$  band. It is suggested that the main mechanism for the occurrence of two-phonon progressions consists in the direct coupling of the incident photon to a two-phonon state via the second-order dipole moment operator. © 2000 Elsevier Science B.V. All rights reserved.

Transition metal compounds (TMC), especially oxides and halides, are today the object of numerous studies on the electron-electron interaction, metalinsulator transitions and polaron formation up to the recent interest in the high-temperature superconductors [1]. For many of these compounds the band picture of electrons fails when the various interactions neglected in the band calculations become larger than the 3d level bandwidth, such as the non periodic potentials, the electron-electron interaction and the electron-phonon coupling. The electron correlation becomes larger as the nuclear charge increases in the 3d elements and the ionic radii in the six-coordinated site becomes smaller, increasing the effective electron density. The metal-insulator transition often appears at both ends of the 3d period, that is, around Ti, V, Ni and Cu, and the magnetic insulators (Mott-Hubbard or charge transfer insulators) are found along the period.

The electron correlation is not so large in the 4d and 5d elements and for most of their compounds (oxides) the band picture seems to work rather well [2].

In TMCs the effect of the electron-phonon (ep) interaction appears as temperature dependent resistivity and superconductivity in metals, while in insulating ionic compounds it determines the polaron formation and the multiphonon fine structures observed in absorption or emission spectra. Among TMCs, the layered crystals with CdCl<sub>2</sub> (C19) or CdI<sub>2</sub> (C6) structure form an ample class of binary compounds, and several of them, involving transition metals, also present interesting magnetic properties. A great success of the spectroscopy of TM ions has been the explanation of the complex absorption structures occurring in the near infrared and visible range of the spectrum in terms of electronic transitions between the d levels split by the crystal field (CF) of the surrounding ions [3].

The existence of a CF in transition metal halides (TMH), i.e., the dependence of the TM ion electronic

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energy on the positions of the neighbour ions, implies in general an important electron-phonon interaction. The most evident and primary effect of the ep coupling is represented by the multiphonon structures observed in the optical absorption spectra of TMHs. These electronic excitations can be classified on the basis of the exciton polaron model [4] as vibronic excitons with small excitations transfer. The observed phonon progressions are in fact reminiscent of those predicted theoretically for small Huang-Rhys factors  $S_0$  ( $S_0 < 3$ ) and small exciton bandwidth (B < 1). The situation is similar to that occurring for localized centres in semiconductors and insulators [5]. The only difference is that these complex elementary excitations may interact with phonons via different mechanisms, due to the two exciton degrees of freedom. In fact, phonons can interact with excitons either through the centre-of-mass translation or through the hole-electron internal motion. Depending on which interaction is dominant, one can have either phonon-assisted processes (in semiconductors) or trapped excitons (in alkali halides), which interact with phonons in the same way as in local centres [5,6].

In layered TMHs, for example, the ep interaction yields in general a complex vibronic structure observed in many CF bands [7]. The quasi-molecular nature of these crystals, due to their low dimensional structure and reduced ionicity [8], results in a flat dispersion of both d-d excitons and optical phonons (vibronic excitons with small excitation transfer) [4]. This allows for the experimental observation of sharp phonon progressions in the absorption spectra of  $d^n + d^n$  parity forbidden transitions. Therefore it appears that the occurrence of such phonon progressions is a general phenomenon to be considered when analysing the visible and infrared spectra of TMHs and have indicated the need of knowing quantitatively the lattice dynamics of layer structures [9,10]. Moreover, from these structures one can learn much on the dynamics of the excited states. It is known that when the ep interaction is given by a purely orbital one-electron operator, a vanishing first-order linear coupling is expected between an ideal isoconfigurational (phononassisted) electronic transition and even parity phonons. Second-order phonon progressions would then be predicted in the sidebands of isoconfigurational transitions.

In intra-configurational transitions of TMHs with *half-filled* shells  $[d^3(t_{2g}); d^5(t_{2g}^3e_g^2); d^8(e_g)]$  the orbital ep coupling vanishes to first order for the Wigner–Eckart theorem [3]. In particular, if the states have a half-filled subshell configuration such as  $t_{2g}^3$ , one may show the calculation of the matrix elements for a low-symmetry potential  $V(\underline{\Gamma})$ ,

$$\left\langle t_{2g}^3 S\Gamma \left\| V(\underline{\Gamma}) \right\| t_{2g}^3 S\Gamma' \right\rangle \neq 0 \quad (\Gamma \neq \Gamma'), \tag{1}$$

only for the combinations

$$S\Gamma = {}^{2}\mathrm{E}, {}^{2}\mathrm{T}_{1}$$
 and  $S\Gamma' = {}^{2}\mathrm{T}_{2},$ 

and vice versa. Similarly, for the  $e_g^2$  configuration, one finds that

$$\langle e_g^2 S \Gamma \| V(\underline{\Gamma}) \| e_g^2 S \Gamma' \rangle \neq 0 \quad (\Gamma \neq \Gamma')$$
 (2)

only for the combinations

$$S\Gamma = {}^{1}E$$
 and  $S\Gamma' = {}^{1}A_{1}$ ,

and vice versa. The group-theory results in Eqs. (1) and (2), valid for the  $t_{2g}^3$  and  $e_g^2$  configurations, indicate which are the expected electronic bands likely to be observed in experiments. As for the  $t_{2g}^n e_g^m$  configuration, further inspection of the matrix elements for the case n + m = 5 (case: n = 3, m = 2) shows again that the only allowed CF transitions are the ones listed in Table 1.

Thus, a second-order progression is expected to be the basic vibronic structure, provided that also the spin-dependent ep interaction (via the phonon modulation of spin–orbit coupling) be zero. Time ago we have reported a clear evidence of two-phonon progressions, due to the second-order linear electron–phonon operator, in NiCl<sub>2</sub> and NiBr<sub>2</sub> crystals [d<sup>8</sup>(e<sub>g</sub>) configuration], by comparing the phonon structure observed in the <sup>3</sup>A<sub>2</sub>(F) + <sup>1</sup>E(D) CF bands with the Raman spectra measured on the same samples [11]. The vanishing of the spin-dependent first-order electron–phonon interaction was then shown to be a necessary condition for observing prominent second-order phonon structures in the intra-configurational transitions observed in these compounds.

The evidence of pure two-phonon progressions observed in late TMCs (i.e., in nickel and manganese dihalides) has then suggested to verify whether the same phenomenon may be observed in early TMHs, where a different type of electronic structure can

Electronic configuration	Electronic transitions	
	Predicted	Observed
$(t_{2g}^3) 3d^3 (V^{2+}; Cr^{2+}3+)$	${}^{4}A_{2}(F) \rightarrow {}^{2}E(G)$	$^{2}E(G)$ in VCl <sub>2</sub> ; VBr <sub>2</sub>
$(t_{2g}^3, e_g) 3d^4 (Cr^{2+}; Mn^{3+})$	${}^{5}E(D) \rightarrow {}^{3}E(H), {}^{3}A_{1}(G), {}^{3}A_{2}(F), {}^{3}E(D)$	${}^{3}A_{1}(G), {}^{3}A_{2}(F)$ in CrBr <sub>2</sub>
$(t_{2g}^{3} e_{g}^{2}) 3_{d}^{5} (Mn^{2+}; Fe^{3+})$	${}^{6}A_{1}(S) \rightarrow {}^{4}A_{1}(G), {}^{4}E(G), {}^{4}E(D)$	<sup>4</sup> E(G) in MnX <sub>2</sub> ; <sup>4</sup> E(D) in MnCl <sub>2</sub>
$(e_g^2) 3d^8 (Ni^{2+})$	${}^{3}A_{2}(F) \rightarrow {}^{1}E(D), {}^{1}A_{1}(G)$	${}^{1}E(D)$ , ${}^{1}A_{1}(G)$ in NiCl <sub>2</sub> and NiBr <sub>2</sub>

Table 1 Electronic transitions where possible second-order phonon transitions are predicted (only for  $\Delta S = 0, 1$ )

occur, owing to a stronger covalence and a lower electronic correlation of the early transition metal compounds [12,13]. Moreover, as said before, the occurrence of a pure two-phonon progression is a rather rare case, since the configurational mixing in the CF levels can switch on a weak first-order ep coupling and mask the two-phonon contribution. Nevertheless, the theoretical prediction of a secondorder structure often provides a key of interpretation for the complicated phonon structures which have been often observed in other 3d-metal compounds. Such a selection rule is fulfilled by the transitions listed in Table 1, where it is shown which second-order phonon progressions are possible.

This Letter is devoted to the optical study of the interesting phonon structures measured in the CF spectrum of newly grown materials, such as the layered vanadium and chromium dihalides. The special case of the electronic  $3d^4(t_{2g}e_g)$  configuration present in CrBr<sub>2</sub> crystals has been in particular considered, since in it, despite the unfilled  $e_g$  semi-shell, a vanishing ep interaction for some transitions between monoclinally split levels has been found. This work follows a similar experimental study on the optical effects of the magnon structures observed in the CF region of Fe dihalides at low temperature [14].

Crystals of VCl<sub>2</sub>, VBr<sub>2</sub> and CrBr<sub>2</sub> have been grown from the vapour phase, using pure elements as starting materials. Usually the crystals grow in the form of large, thin platelets (ca.  $10 \times 10 \times 0.1 \text{ mm}^3$ ) perpendicular to the *c*-axis. A flow-system method has been in general used, where the halogen gas carried by dry nitrogen attacks the pure powdered metal at growing temperature typical for each crystal (500–800°C). In particular, the crystals of CrBr<sub>2</sub> were obtained by reduction (with very pure H<sub>2</sub>) of a weighted quantity of  $CrBr_3$  in a U tube at 350–400°C for 6–10 h. White tiny crystals are thus obtained. They are rather hygroscope and rapidly oxidised in air. Hygroscope samples have been treated in a glow-box, filled with nitrogen or argon gas, in order to prevent deterioration due to moisture. In the visible region a double-beam Cary 14 spectrophotometer was used and the temperature was checked by a CLST sensor by Oxford Instruments.

The crystals under consideration belong to the  $D_{3d}^3$ space group, with the cation at a  $D_{3d}$  site surrounded by a octahedral cage of halogen ions. Since the trigonal distortion of the ligand field is small, the electronic levels can still be classified in terms of the cubic  $(O_h)$  irreducible representations. On the contrary, the zone centre phonons strongly reflect the crystal anisotropy and have to be labelled by the trigonal irreducible representations. For example, vanadium dihalides crystallize in a layered structure of the CdI<sub>2</sub> type and belong to the trigonal space group  $D_{3d}^3$ . This structure consists of hexagonal sheets of metal atoms sandwiched between two hexagonal sheets of anions. The nearest neighbours of a metal atom form a slightly distorted octahedron. A factor group analysis yields four optical modes at the  $\Gamma$ point,  $A_{1g} + E_g + A_{2u} + E_u$ , i.e., two Raman-active modes (even) and two infrared-active (odd) modes. Owing to their structures and their reduced ionicity, these crystals present rather flat dispersion curves associated with the optical mode Eg and a sharp peak at  $\omega(E_g)$  in the  $E_g$  projected phonon density is in general expected. The CrBr2 compound belongs to the space group  $C_{2h}^3$  [15] and is a special case.

The experimental results on vanadium and chromium dihalides are now presented and discussed in the light of the theoretical concepts exposed before.



Fig. 1. Two-phonon progression observed in VCl<sub>2</sub> crystals in the crystal field  ${}^{2}E(G)$  and  ${}^{1}T_{2}(G)$  bands at 5 K.



Fig. 2. Two-phonon progression observed in VBr<sub>2</sub> crystals in the crystal field band <sup>2</sup>E(G) at 5 K.

Figs. 1 and 2 show the  ${}^{2}E(G)$  and  ${}^{2}T_{2}(G)$  absorption bands of VCl<sub>2</sub> and VBr<sub>2</sub> compounds at 5 K, respectively. These bands are well separated by a deep minimum around 11.900 and 12.100 cm<sup>-1</sup>. The spinorbit coupling accounts for the splitting observed in the  ${}^{2}T_{2}(G)$  band, but neither the spin-orbit coupling

nor the trigonal field perturbation can lift the degeneracy of the  ${}^{2}E(G)$  band [3]. While the small splitting of 84 cm<sup>-1</sup> in VCl<sub>2</sub> and 122 cm<sup>-1</sup> in VBr<sub>2</sub> could also be due to optical magnons (quickly washed out by increasing temperature), the broad sidebands observed above the  ${}^{2}E(G)$  band cannot have but a phonon origin.



Fig. 3. The crystal field spectrum of  $CrBr_2$  crystals at 5 K. The two-phonon progression observed in the  ${}^{3}A_1(G) + {}^{3}A_2(F)$  electronic band is reported in the insert.

In fact, the spacing of 404 and 260  $\text{cm}^{-1}$  corresponds quite well to twice the respective Raman Eg frequencies [10,16]. In principle, all frequencies associated with the above transitions should be slightly different and shifted with respect to the Raman frequencies, due to the different relaxation of the excited states. Firstand second-order phonon spectra have been also studied by Bauhofer et al. [16], who have measured twophonon infrared absorption spectra and discussed the mechanisms responsible for the two-phonon infrared absorption in polar crystals. While the first mechanism they discuss is the same which is active in our compounds (the direct coupling of the photon to a twophonon state via the second-order dipole moment operator), they also considered the effect of the cubic anharmonicity, which can couple the incident photons with transversal optical lattice modes and yield the phonon sidebands observed in the optical spectra.

Nice one-phonon progressions have been also observed in MnCl<sub>2</sub> and MnBr<sub>2</sub> in the CF bands  ${}^{4}T_{3}(D)$ and  ${}^{4}E(D)$  [7,17] and in  ${}^{4}E(G)$ ,  ${}^{4}A_{1}(G)$  in MnI<sub>2</sub> [18]. As for the intra-configurational transitions, the  ${}^{6}A_{1}(S) \rightarrow {}^{4}E(G) + {}^{4}A_{1}(G)$  transition in both compounds shows a puzzling phonon structure, together with the notable common feature that the spacings between the first two sharp peaks are nearly twice the Raman  $E_{g}$  frequencies (see Fig. 2 in [17]). However, these examples will not discussed any more, since they have been already presented in detail in previous works [7,17,19].

While in  $3d^3$ ,  $3d^5$  and  $3d^8$  configurations a vanishing first-order ep coupling descends from the group theory [3] for the transitions shown in Table 1, in the  $3d^4$  configuration, this occurs accidentally. For this reason, the special case of the  $d^4(t_{2g}e_g)$  configuration in CrBr<sub>2</sub> (space group  $C_{2h}^3$  [15]) has been considered. Thus, good quality CrBr<sub>2</sub> crystals have been grown and the crystal field spectrum has been measured and shown in Fig. 3. The fitting of the observed transitions to the octahedral crystal field diagram, including the spin–orbit coupling [20], has given a CT parameter  $10 \text{ Dq} \sim 12000 \text{ cm}^{-1}$ . Only one vibronic structure was observed in the whole spectrum. This structure is associated with the nearly degenerate transitions  ${}^3A_2(F)$ ,  ${}^{3}A_{1}(G)$  and presents a spacing of 306 cm<sup>-1</sup>. As shown in Table 4 of Ref. [10], this frequency scales quite well with twice the Raman A<sub>1g</sub> frequency of VBr<sub>2</sub> (316 cm<sup>-1</sup>) and MnBr<sub>2</sub> (302 cm<sup>-1</sup>) and therefore it is suggested that it corresponds to a second-order vibronic structure of the same kind shown in vanadium, manganese and nickel halides.

In conclusion, it has been shown that, owing to the small dispersion of the phonon branches, it is possible to observe sharp two-phonon progressions in the crystal field spectrum of layered transition metal halides. It is also claimed that the main mechanism for the occurrence of this exceptional case (onephonon progressions are the rule) consists in the direct coupling of the incident photons to a two-phonon state via the second-order dipole moment.

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