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Evidence of two-phonon vibronic progressions in layered 3*d*-metal dihalides

G. Benedek*
Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 80, Federal Republic of Germany

I. Pollini
Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Istituto di Fisica dell'Universitá, Milano, Italy

L. Piseri and R. Tubino
Istituto di Chimica delle Macromolecole del Consiglio Nazionale delle Ricerche, Milano, Italy

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Experimental evidence of two-phonon vibronic progressions due to second-order linear electron-phonon interactions is obtained in $NiCl_2$ and $NiBr_2$ crystals, by comparing the phonon structure observed in $^3A_2(F) \to {}^1E(D)$ transition with Raman data. The vanishing of the spin-dependent first-order electron-phonon interaction is shown to be a necessary condition for observing prominent second-order phonon structures in isoconfigurational crystal-field transitions. According to this rule we predict and discuss the appearance of second-order progressions in other *d*-metal layered compounds.

I. INTRODUCTION

Electron-phonon (*e*-*p*) interaction in layered transition-metal compounds presents several stimulating aspects, such as the Raman scattering by optical phonons and by low-lying electronic excitations,[1-3] the magnon–acoustic-phonon hybridization,[4-6] the dynamical Jahn-Teller effect,[2,7] the coupling of optical phonons to charge-density waves,[8] and the complicated vibronic structures observed in crystal-field transitions.[9-12]

An interesting case, frequently occurring in transition-metal as well as in rare-earth compounds, is that of isoconfigurational transitions. When the *e*-*p* interaction is given by a purely orbital one-electron operator, a vanishing first-order linear coupling is expected between an ideal isoconfigurational (phonon-assisted) electronic transition and even-parity phonons. Second-order phonon progressions would then be predicted in the sidebands of isoconfigurational transitions.[13]

Until now, no evidence of second-order progressions was found, however. In general, even when the final state is conjectured to have a weak configurational mixing with other terms, two other facts are against the observability of a resolved second-order phonon structure: (i) The two-phonon density involved in the second-order processes is usually too broad, and (ii) the spin-dependent part of the *e*-*p* coupling, occurring via spin-orbit interaction, can still given an appreciable first-order contribution also in isoconfigurational transitions. Both these obstacles can nevertheless be less severe, if not absent, in transition-metal layered compounds.

The crystals under consideration belong to the D_{3d}^5 space group, with the cation at a D_{3d} site surrounded by a distorted octahedral cage of halide ions. Since the trigonal distortion of the ligand field is small, the electronic levels can still be classified in terms of cubic (O_h) irreducible representations. On the contrary the zone-center phonons strongly reflect the crystal anisotropy and have to be labeled by trigonal (D_{3d}) irreducible representations. Owing to their structure and their reduced ionicity, these crystals present rather flat dispersion curves associated with the optical E_g mode, and a sharp peak at $\omega(E_g)$ in the E_g-projected phonon density is expected. For instance, in $FeCl_2$ Pasternak[14] predicts an E_g-branch dispersion as small as 18 cm^{-1}, and a similar situation holds for the other compounds.[15] Furthermore some isoconfigurational transitions occur between multiplets of the ^{2S+1}A, ^{2S+1}E, or ^1T type, where the spin-orbit induced *e*-*p* interaction vanishes for symmetry reasons.

In this paper we give a first evidence of two-phonon vibronic progressions, observed in $NiCl_2$ and $NiBr_2$, originated by the second-order linear *e*-*p* interaction. We propose a simple explanation based on the simultaneous vanishing of orbital and spin-dependent first-order *e*-*p* coupling. Ac-

TABLE I. Transitions where observable second-order phonon progressions are predicted (only for $|\Delta S| = 0, 1$).

Configuration	Transitions
$d^3(V^{2+}, Cr^{3+})$	$^4A_2(F) \to {}^2E(G)$
$d^4(Cr^{2+}, Mn^{3+})$	$^5E(D) \to {}^3E(H), {}^3A_1(G), {}^3A_2(F), {}^3E(D)$
$d^5(Mn^{2+}, Fe^{3+})$	$^6A_1(S) \to {}^4A_1(G) + {}^4E(G), {}^4E(D)$
$d^8(Ni^{2+})$	$^3A_2(F) \to {}^1E(D), {}^1A_1(G)$

cording to this rule we then predict and discuss the appearance of second-order phonon structures in other d-metal layered compounds (Table I).

II. SECOND-ORDER PHONON PROGRESSIONS IN Ni DIHALIDES

Crystal-field transitions in $NiCl_2$ and $NiBr_2$ were first reported by Kozielski *et al.*[9] Vibronic progressions were observed within the bands $^3T_2(F)$ and $^3T_1(F)$, and associated with trigonal E_g and A_{1g} optical vibrations, respectively.[10] Such an assignment, however, appears now to be incorrect for two reasons.

First, the transition $^3A_2(F, e^2) \rightarrow {}^3T_1(F, t_2^2)$ implies a large configurational change, namely a strong e-p coupling, which would prevent the observation of sharp phonon progressions. Indeed a refined analysis of crystal-field spectra taking into account trigonal distortion effects shows that the sharp phonon progression belongs to the spin-forbidden isoconfigurational transition $^3A_2(F, e^2) \rightarrow {}^1E(D, e^2)$,[12] which in these Ni compounds fall just on the high-energy side of the $^3T_1(F)$ band. Consequently, we have found a more accurate description of the true $^3T_1(F)$ band at 5 K (same experimental procedure as Ref. 9), finding in both crystals only weak progressions with the same spacing already observed in the $^3T_2(F)$ band (Fig. 1).

The second reason is that the two vibronic frequencies ($\omega = 251$ cm^{-1} and 335 cm^{-1} for $NiCl_2$; 160 cm^{-1} and 202 cm^{-1} for $NiBr_2$) if assigned to fundamental even-parity phonons, appear to be exceedingly large when compared with the correspondent pairs in $MnCl_2$ and $MnBr_2$,[10] and with those of other similar compounds investigated by Raman spectroscopy.[1,2]

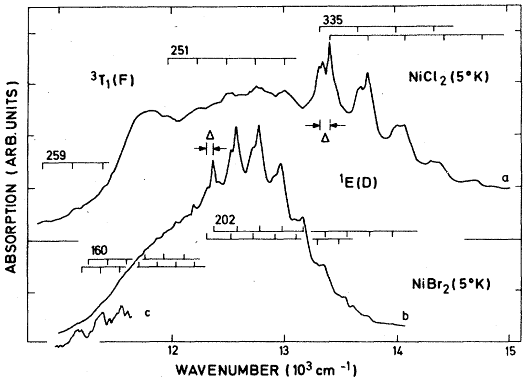

FIG. 1. $^3T_1(F)$ and $^1E(D)$ absorption bands of $NiCl_2$ (curve *a*) and $NiBr_2$ (curve *b*) at 5 K. The low-energy side of $NiBr_2$ spectrum is shown × 5 magnified after subtraction of a Poissonian $\propto S^n/\Gamma(n+1)$ (curve *c*). A good fit of the $^3T_1(F)$ band is obtained with a Huang-Rhys factor $S=10.3$, $n=(\omega-\omega_0)/160$ cm^{-1}, and a pure exciton-phonon line at $\omega_0=10\,700$ cm^{-1}. The values 335 and 202 cm^{-1} refer to the first interval, as the spacing reduces for increasing order as an effect of multiple phonon density convolutions. The average spacing is 320 and 190 cm^{-1}, respectively; clearly, in our context the first spacing is meaningful.

As the cation masses of these compounds are nearly equal, large variations in vibrational frequencies would only be justified by large changes in force constants. This is not expected on the basis of the similarity of electronic and crystal structure. Moreover, excited-state relaxation, which allows the vibronic frequencies to be different from Raman frequencies, is rather small in crystal-field isoconfigurational transitions (only a few wave numbers), and can not explain the case of Ni dihalides.

In order to clarify this point, we have measured room temperature Raman spectra of $NiCl_2$ and $NiBr_2$ and, for sake of comparison, also those of Co, Fe, and Mn dichlorides and dibromides under equivalent experimental conditions. All crystals were grown from vapor phase by the flow system. Unpolarized Raman spectra, with incident beam parallel to the c axis, were excited by the lines at 647.1 nm (Fe and Ni dihalides) and 488.0 nm (Mn and Co dihalides) of an Ar-Kr laser of the coherent radiation (Model 52 MG) and registered at 90° with a Jarrell-Ash 25-300 spectrophotometer equipped with a photomultiplier IITFW-130 (Fig. 2). As expected, only regular (and small) frequency changes occur in the chloride and bromide series (Fig. 2). In particular, the A_{1g} Raman frequencies of $NiCl_2$ and $NiBr_2$ ($\omega = 260$ cm^{-1} and 168 cm^{-1}, respectively) are very close to the vibronic frequencies of the $^3T_2(F)$ and $^3T_1(F)$ bands, which are thus definitely assigned to A_{1g} symmetry. On the other hand the vibronic frequency of the band $^1E(D)$ is seen to be nearly exactly twice the Raman E_g frequency in both crystals.

We conclude that the phonon structure associated with the $^1E(D)$ isoconfigurational is the first experimental evidence of a two-phonon $E_g \times E_g$ progression. This is possible because in $NiCl_2$ and $NiBr_2$ the convolution of the E_g branches with themselves yields a two phonon density width of about 60 and 40 cm^{-1}, respectively.[15] Thus two-phonon progressions can be resolved, in the weak-coupling limit, up to the fifth or sixth order.

We note also that the $^1E(D)$ vibronic structure consists of at least two identical progressions with different origins. The origins are shifted by $\Delta = 72$ and 48 cm^{-1} for $NiCl_2$ and $NiBr_2$, respectively, which corresponds strikingly to the frequency difference between ungerade modes, $\omega(A_{2u}, \mathrm{TO}) - \omega(E_u, \mathrm{TO}) = 68$ and 49 cm^{-1}, as mea-

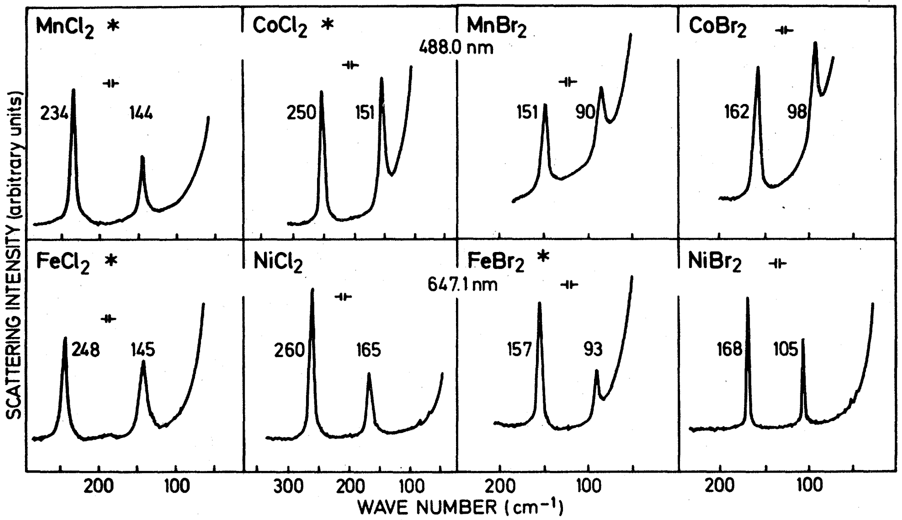

FIG. 2. Raman spectra of Mn, Fe, Co, and Ni dichlorides and dibromides at room temperature. At each peak the correspondent frequency in cm^{-1} is reported. Low-temperature spectra of the compound marked by an asterisk have been already reported by Lockwood and co-workers (Refs. 1–3).

sured in far-infrared transmission spectra.[12] This could be interpreted in terms of a single forbidden electronic transition assisted by the two polar phonons of trigonal A_{2u} and E_u symmetry. We note that the difference between A_{2u} and E_u TO frequencies is here considered as positive, unlike Lockwood's attribution giving $\omega(E_u, \mathrm{TO}) > \omega(A_{2u}, \mathrm{TO})$.[1] Indeed the more accurate and systematic infrared transmission data of Ref. 12 yield strong evidence that Mn, Fe, Co, and Ni dichlorides and dibromides all have the TO A_{2u} mode above the E_u TO mode. The same is true for other similar compounds recently investigated by van der Valk and Haas, who give also a solid theoretical justification.[16]

III. SELECTION RULES

The theoretical explanation of the two-phonon progressions starts from the simple argument that the first-order e-p interaction for the ${}^3A_2(F, e^2) \rightarrow {}^1E(D, e^2)$ transition, here split into orbital and spin-dependent parts[13]

$$L_1^{(o)} + L_1^{(s)} = ({}^1E, e^2 \,|H_{e\text{-}p}^{(o)} + H_{e\text{-}p}^{(s)}|\, {}^1E, e^2) - ({}^3A_2, e^2 \,|H_{e\text{-}p}^{(o)} + H_{e\text{-}p}^{(s)}|\, {}^3A_2, e^2)\,, \tag{1}$$

is zero. In fact the orbital part of the e-p Hamiltonian, $H_{e\text{-}p}^{(o)}$, due to phonon-induced distortion of the ligand field, is zero because of the isoconfigurational character of the transition, while the spin-dependent part $H_{e\text{-}p}^{(s)}$, essentially due to the phonon modulation of the spin-orbit constant, does not affect E and A multiplets.

On the other hand, the second-order e-p contribution, mainly due to phonon-induced mixing of ground and excited states with the closest isospin levels[17]

$$L_2^{(o)} = \frac{|({}^1E, e^2 \,|H_{e\text{-}p}^{(o)}|\, {}^1T_2, et_2)|^2}{E({}^1E) - E({}^1T_2)} - \frac{|({}^3A_2, e^2 \,|H_{e\text{-}p}^{(o)}|\, {}^3T_2, et_2|^2}{E({}^3A_2) - E({}^3T_2)} \tag{2}$$

is nonvanishing. Owing to the different configurations of the admixed states, the matrix elements of $H_{e\text{-}p}^{(o)}$ in Eq. (2) reduce to the one-electron matrix element $(e\,|H_{e\text{-}p}^{(o)}|\,t_2)$. This is nonvanishing only for $H_{e\text{-}p}^{(o)}$ transforming like T_{1g} and T_{2g} irreducible representations. Therefore, only shear deformations of the ligand octahedral cage, namely trigonal E_g phonons, give second-order progressions.

If we accept the idea that the observability of second-order progressions depends upon the lack of first-order interaction, we can predict second-order progressions for those transitions where both orbital and spin-dependent e-p interactions $L_1^{(o)}$ and $L_1^{(s)}$ are simultaneously zero. It is worth noting that $L_1^{(s)}$ must be taken into account because its contribution, when not vanishing for symmetry reasons, can be larger that the residual orbital e-p interaction maintained in isoconfigurational transitions by configurational mixing. $L_1^{(s)}$ can be evaluated for the $\bar{\Gamma}$th spin-orbit level of the ${}^{2S+1}\Gamma$ multiplet of configuration α as

$$L_1^{(s)} = \Delta_{g\rightarrow e}\Big(\alpha S\Gamma, \bar{\Gamma}\,\Big|\left(\frac{\hbar}{2M\omega_\gamma}\right)^{1/2} \frac{\partial\lambda(\alpha S\Gamma)}{\partial u_\gamma}\vec{\mathrm{S}}\cdot\vec{\mathrm{T}}\,\Big|\,\alpha S\Gamma, \bar{\Gamma}\Big) = \left(\frac{\hbar}{2M\omega_\gamma}\right)^{1/2} \frac{\partial \ln\zeta}{\partial u_\gamma}\Delta_{g\rightarrow e}\lambda_{\bar{\Gamma}}(\alpha S\Gamma)\,, \tag{3}$$

where $\Delta_{g\rightarrow e}$ means the difference between excited- and ground-state expressions, $\lambda(\alpha S\Gamma)\vec{\mathrm{S}}\cdot\vec{\mathrm{T}}$ is the operator equivalent of the spin-orbit interaction, $\lambda_{\bar{\Gamma}}(\alpha S\Gamma)$ its eigenvalues, and ζ is the spin-orbit constant for the d orbital of t_2 symmetry[17]; ω_γ,

u_γ, and M are frequency, displacement, and effective mass for the phonon γ. The phonon perturbation of ζ occurs via the phonon modulation of the overlap between d orbitals and π-like combinations of p ligand orbitals. In Misetich-Buch approximation such a modulation is just an additive expression of individual ligand ion contributions,[17] and therefore, to first-order in u_γ, only totally symmetric phonons give a nonvanishing $L_1^{(s)}$. Assuming for the overlap a Born-Mayer dependence on the interionic distance r, namely $\exp(-r/\rho)$ with $\rho \simeq 0.3$ Å,[15] we have

$$\frac{\partial \ln\zeta}{\partial u_\gamma} \simeq \frac{2}{\rho}\left(\frac{\zeta_0}{\zeta} - 1\right), \tag{4}$$

where ζ_0 is the free-ion spin-orbit constant. The departure of ζ from ζ_0 can be appreciable for ligand ions heavier than F^-. Exemplary values obtained from fitting crystal-field spectra are $\zeta_0/\zeta - 1 = -0.3$ for $NiCl_2$ and $NiBr_2$,[9] and -0.57 for VI_2.[18] Since $(\hbar/2M\omega_\gamma)^{1/2}$ is typically $10^{-1}\rho$ and $\Delta_{g\to e}\lambda_{\bar{\Gamma}}$ is of the order of ζ, the range of $L_1^{(s)}$ is 10 to 10^2 cm^{-1}, namely only one order of magnitude less than the orbital e-p interaction in crystal-field transitions with one-electron configurational change (where $L_1^{(o)} \simeq D_q$).

Moreover, $L_1^{(s)}$ has the same magnitude of $L_2^{(o)}$, for $(e|H_{e\text{-}p}^{(o)}|t_2)$ is also of the order of D_q ($\simeq 700$ cm^{-1}) and both energy denominators in (2) are $\simeq 6000$ cm^{-1}. Thus, *in order to resolve a second-order structure, the spin mechanism should be absent.*

Looking at the values of $\lambda_{\bar{\Gamma}}(\alpha S\Gamma)$ for the various multiplets,[17] we see that $L_1^{(o)}$ and $L_1^{(s)}$ are never simultaneously zero for d^2, d^6, and d^7 configurations (ground states $^3T_1(F)$, $^5T_2(D)$, and $^4T_1(F)$, respectively), whereas in d^3, d^4, d^5, and d^8 this occurs for the few transitions listed in Table I.

IV. DISCUSSION

Except for d^4, for which we do not know any detailed study of vibronic sidebands, the transitions listed in Table I are just those where some structure attributable to an $E_g \times E_g$ progression is argued. In a d^5 configuration the $E_g \times E_g$ progression of $^6A_1(S) \to {}^4E(G)$ transition at 22090 cm^{-1} is rather evident in MnI_2,[18] with a spacing of 140 cm^{-1}, and also in $MnCl_2$ and $MnBr_2$ some E_g progressions with strong second-order character are identified.[12] An $E_g \times E_g$ progression, superimposed on a stronger first-order A_{1g} series, is found also in the $^6A_1(S) \to {}^4E(D)$ transition of $MnCl_2$ at 28104 cm^{-1} with a spacing of 272 cm^{-1},[11] but no analog is detected in $MnBr_2$ and MnI_2.

In the d^3 configuration the $^4A_1(F) \to {}^2E(G)$ transition, observed by Van Erk in VI_2,[18] shows at 5.3 K a sequence of two sharp peaks spaced by 212 cm^{-1} which in Van Erk's accurate crystal-field analysis remained unexplained. Analogous but broader structure is observed at the same temperature in VBr_2 and VCl_2, with a spacing of 254 and 404 cm^{-1}, respectively.[19] These values correspond reasonably well to twice the respective E_g Raman frequencies (90 cm^{-1} in VI_2, 125 cm^{-1} in VBr_2, and 198 cm^{-1} in VCl_2.)[20] The discrepancy of VI_2 is somewhat disturbing. Nonetheless, a well defined first-order progression is found in the $^2E(H)$ band at 20 400 cm^{-1}, with a spacing of 107 ± 2 cm^{-1},[19] exactly half the second-order spacing found in $^2E(G)$. Moreover, when dealing with a second-order spacing, one should keep in mind the shift due to the combined effects of anharmonic renormalization of the two-phonon state energy, phonon-density convolution, excited-state relaxation, etc., all quantities about which we have at the moment only a rough idea.

With such flexibility, the spacing of 182 cm^{-1} found in the $^3A_2(F) \to {}^1A_1(G)$ of $NiBr_2$ (Ref. 21) could also be attributed to an $E_g \times E_g$ progression. This is supported by the fact that the same transition is now detected also in $NiCl_2$,[12] again with a many-phonon spacing of 320 cm^{-1}, which is very close to that of the $^1E(D)$ transition.

Finally we note that no $E_g \times E_g$ series is observed in isoconfigurational transitions of d^6 and d^7 configurations (Fe and Co dihalides),[12] where the spin-dependent e-p interaction plays an important role in the ground state.[1-3]

Even if all the above examples strengthen the evidence of second-order phonon structures and, indirectly, of the role played by the spin-dependent e-p interaction, the observation of pure two-phonon series like those of Ni dihalides is rather exceptional. For example, in Mn compounds they are always superimposed on sharp first-order progressions, and often completely overshadowed.

Indeed the above selection rules are a sort of a zero-order approximation. In practice, each level is more or less coupled to levels of different configuration via a two-electron Coulomb repulsion, spin-orbit interaction and trigonal distortion field. All these types of interconfigurational mixing obviously yield nonvanishing contributions to $L_1^{(o)}$. The question is whether and when such contributions are still smaller than $L_2^{(o)}$. A theoretical quantitative answer, although quite difficult, is nevertheless worth being approached in a future work, particularly in order to check the validity of the first-order approximation currently used for the e-p interaction in several problems. From the experimental point of view, as soon as Raman scattering in resonance with transitions as weak as those between crystal-field levels will be feasible, one would have a direct test of the present interpretation. In fact the quenching of first-order e-p coupling should enhance, in resonance, the ratio of second-order to first-order E_g-mode Raman amplitudes.

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*Permanent address: Gruppo Nazionale di Struttura della Materia del C.N.R., Istituto di Fisica dell' Università, Milano, Italy.

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