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MAGNETIC VIBRATIONAL RAMAN SCATTERING OF KI DOPED WITH F CENTRES

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Résumé. — Nous avons étudié la diffusion Raman, sous champ magnétique, de KI dopé avec des centres F. L'interprétation des spectres exige la prise en compte du couplage spin-orbite de l'état excité 2P du centre F. Les principales caractéristiques de ces spectres sont au moins qualitativement en accord avec le modèle simple de l'approximation quasi résonante.

Abstract. — We have studied the Raman scattering under magnetic field by F centres in KI. The spin orbit coupling of the 2P excited state must be taken into account in order to explain the observed spectra. The simple model of the quasi-resonant approximation provides a reasonably exact description of the observed features.

Experimental studies of Raman scattering by KI doped with F centres have been previously published [1, 2]. We recall that in the off resonance approximation the active modes are of Γ_1^+ , Γ_3^+ and Γ_5^+ symmetry. At 10 K the spectra show a very intense and sharp line at 96 cm^{-1} , which has been attributed to a Γ_1^+ resonant optical mode. Indeed the calculation predicts a strong resonant Γ_1^+ mode, but is unable to account for the 96 cm^{-1} line which appears in the Γ_3^+ and Γ_5^+ spectra. However we have recently shown that the spin-orbit interaction in the excited state could explain rather satisfactorily this feature [2].

In order to check this hypothesis we have performed Raman scattering experiments in a magnetic field, which turns out to be the relevant perturbation for this purpose.

The KI crystal doped with F centres (the maximum of the absorption band lies at 660 nm at 10 K) was excited by a dye laser which could be tuned between 590 and 625 nm. The light power could be ranged between 60 and 300 mW. A magnetic field of 4.5 T was provided by a superconducting magnet and the experiments were performed at 1.7 K. A sketch of the experimental arrangement is reported in the insert of figure 1. The directions of the incident and scattered beams were parallel to the four-fold Ox and Oz axes

FIG. 1. — The Raman scattering of KI doped with F centres for the experimental arrangement sketched top right. X, Y, Z, are the four-fold axes of the crystal; the linear polarization of the incident light (E_i), the magnetic field (H) and the direction of the scattered beam were along the Oz axis. In this experiment no analysis of the polarization of the scattered light was performed. Laser wavelength, 620 nm; laser power, 140 mW; slit-width, 3 cm^{-1} . Curve A : Raman scattering without magnetic field. Curve B : Raman scattering under 4.5 T magnetic field.

respectively. The magnetic field was along the Oz axis as was the linear polarization of the incident light.

If the spin orbit coupling in the 2P excited state was neglected, this configuration would only lead to the determination of Γ_5^+ modes. Actually the

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Raman spectrum observed without magnetic field (Fig. 1 curve A) exhibits the 96 cm^{-1} resonant mode and its first overtone at 193 cm^{-1} . The broad band at 130 cm^{-1} has been partially attributed to the optical modes of Γ_5^+ symmetry. When the magnetic field is applied an apparent feature of the experiment turns out to be the splitting of both 96 cm^{-1} mode and its first overtone (Fig. 1 curve B).

This observed feature may be understood in terms of the scheme reported in figure 2. On this figure the ^2S ground state of the F centre is sketched. The application of the magnetic field splits the 0 and 1 vibronic levels into two sub-levels possessing the magnetic quantum numbers $\pm \frac{1}{2}$. Then the Raman spectrum should exhibit three lines. Two of them correspond to transitions involving a spin flip (ν_+ and ν_-) and are separated by $2g\beta H$. The other one which does not involve any spin flip would lie at the same frequency as the original one.

FIG. 2a. — Scheme of the Raman frequencies under magnetic field for a ^2S ground state. Only the two first vibronic levels (0,1) with their magnetic sub-levels ($\pm \frac{1}{2}$) are represented on this figure. ν is the Raman frequency without any magnetic field, $\nu_{\pm}$ are the Raman frequency involving a spin flip. b) Experimental configuration used for the study of the magnetic Raman scattering due to a Γ_1^+ phonon. X, Y, Z are the four-fold axes of the crystal. c) Relative intensities of the three Raman lines for a Γ_1^+ phonon and for the configuration of the figure 2b. $\vec{E}_i$ is the linear polarization of the incident beam; $\vec{E}_s$ is the linear or circular polarization vector of the scattering beam. $n_{\pm}$ are the populations of the magnetic sub-levels of the 0 vibronic ground state.

In order to determine the selection rules corresponding to the configuration of the figure 2b, we have taken into account the spin orbit and the Zeeman interactions. For this purpose we have used the Raman theory developed by Henry [3] and Buchenauer [4] in the *quasi-resonant approximation*. Besides the classical terms only due to electron-lattice coupling, we then obtain second order terms whose magnitude

is proportional to $(C_i C_{so})^2$. C_i and C_{so} are the coupling constants for electron-lattice and spin-orbit interactions in the excited state ^2P . For a Γ_1^+ mode the relative intensities of these latter terms are indicated in figure 2c. The same calculation can be performed in the case of scattering by phonons of Γ_3^+ and Γ_5^+ symmetry. The intensities of the ν_+ and ν_- lines are still proportional to C_{so}^2 but the selection rules depend upon the symmetry of the mode involved and are different from the Γ_1^+ case.

In particular the broadening of the 130 cm^{-1} line can be explained by transitions due to the spin flip. In this case more detailed results could be obtained with the technique of Raman circular intensity differential as reported by Barron [5].

We have then studied the 96 cm^{-1} line according to the state of polarization of the scattered light as is shown in figure 2, and found the following :

1) If $(\vec{E}_i, \vec{E}_s) \equiv (\text{Y}, \text{X})$, no modification of the line appears under magnetic field, in agreement with the selection rules.

2) If $(\vec{E}_i, \vec{E}_s) \equiv (\text{Z}, \sigma_{\pm})$, the results are indicated figure 3. According to the selection rules for a Γ_1^+ mode, the central line (ν) disappears and both ν_+ and ν_- lines are maintained and separated by 7.9 cm^{-1} in good agreement with the theoretical value $2g\beta H = 8.4\text{ cm}^{-1}$. On the other hand, at 1.7 K the two spectra σ_+ and σ_- are observed with nearly equal intensities. The same phenomenon occurs using a 600 nm laser line, i.e. out of the F absorption band, but in the K band. As is obvious from figure 2c, the ground state sub-level populations are not governed by the classical Boltzman law. Such a deviation from the Boltzman equilibrium may be attributed to the long spin-lattice relaxation time and to the spin memory loss during the pumping cycle.

FIG. 3. — Raman scattering of the 96 cm^{-1} resonant mode for the $(\vec{E}_i, \vec{E}_s) \equiv (\text{Z}, \sigma_{\pm})$ configuration of the figure 2. Laser wavelength, 620 nm ; laser power, 140 mW ; slit width, 3 cm^{-1} ; magnetic field, 4.5 T . Curve A : Raman scattering without magnetic field and for a σ_+ or σ_- scattered polarization. Curve B and C : Raman scattering under 4.5 T magnetic field for σ_- and σ_+ scattered polarizations respectively.

Moreover as can be seen in figure 3 a rather strong depolarization (30 %) exists for both ν_+ and ν_- lines. The origin of these effects is not clear, but several explanations can be proposed : for example one can invoke the internal stresses, the hot fluorescence process, or the failure of the off-resonance approximation used in our calculation.

In conclusion, as previously predicted by Buchenauer [4] and Mulazzi [6] the classical selection rules

are not strictly observed when the spin-orbit interaction in the excited state of the F centre is taken into account. Therefore, Raman spectra under magnetic field allow one to test the breaking of selection rules. Such experiments would be interesting in particular for the study of broad bands generally observed in Raman spectra of crystals doped with impurities or defects.

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