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Splitting of the ruby fluorescence under stress

A. Monteil, E. Duval, A. Attar, G. Viliani (*)

Spectroscopie des Solides (**), Université Lyon I, Campus de la Doua, 69622 Villeurbanne, France

and R. Lacroix

Département de Chimie-Physique, Université de Genève, Switzerland

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Résumé. — Un dédoublement de la fluorescence R_1 du rubis est observé quand une pression P est appliquée sur le cristal suivant des directions bien particulières. Il est linéaire en fonction de P^2 en accord avec la théorie. Il provient de la levée de dégénérescence des ions Cr^{3+} situés dans deux sous-réseaux différents.

Abstract. — A splitting of the R_1 ruby fluorescence is observed when a pressure P is applied on the crystal along special directions. It is linear as a function of P^2 , in agreement with the theory. It comes from the lifting of the degeneracy of Cr^{3+} ions located in two different sublattices.

Several works have been published dealing with the uniaxial stress effect on the optical transition of ions such Cr^{3+} [1-4], Co^{3+} and V^{3+} [4-6] in corundum ($\alpha-Al_2O_3$). One of the principal results of the experimental studies is the evidence of a local or internal strain in pure corundum crystal. A theory of the inner elasticity applied to corundum and based on space-group theory was given by Cousins [7]. On the other hand Lacroix *et al.* [8] determined the local strain or the ion displacements which do not contribute to the crystal strain by using the point group method and the elasticity theory by Born and Huang [9].

The effect of a uniaxial stress on the ${}^4A_2 \rightarrow {}^4T_2$ of Cr^{3+} [3], ${}^3A_2({}^3T_1) \rightarrow {}^3T_2$ of V^{3+} [6], and more particularly on the ${}^1A_1 \rightarrow {}^1T_1$ of Co^{3+} [5] zero-phonon absorption lines, shows that the cation sites are separated into two sublattices for certain directions of the stress. The two sublattices which will be called σ -sublattices are different from the E-sublattices separated by an electric field parallel to the trigonal axis.

The separation into two sublattices is easily understood by considering the internal symmetry of the crystal. We notice two different symmetries between cation sites. (1) The cation sites between two adjacent oxygen planes are symmetric by inversion. (2) On the contrary two cation sites on each side of a same oxygen plane are symmetric by π -rotation around a $2\bar{1}10$ axis (or C_2 -axis). Actually, if we consider figure 1, we see that A and B' or B and A' are symmetric by inversion, on the contrary A and B, or A' and B' are symmetric by π -rotation around the C_2 -axis.

(*) Permanent address : Dipartimento di Fisica, Università di Trento, 38050 Povo Trento, Italy.

(**) ERA 442 du CNRS.

Fig. 1. — Projection of the $\alpha\text{-Al}_2\text{O}_3$ lattice on the $(2\bar{1}10)$ symmetry plane showing the different cation sublattices and (x_1, x_2, x_3) referential.

Now if we assume that the x_1 -axis is parallel to a C_2 -axis, x_3 to the C_3 -axis (x_2 is deduced from x_1 and x_3), σ_{12} or σ_{13} external stresses will have opposite effects on sites symmetric by π -rotation around the C_2 -axis, and the same effect on sites symmetric by inversion (stress being itself symmetric by inversion). Therefore cation sites on each side of a same oxygen plane are separated by a σ_{12} or σ_{13} stress. On the contrary, cation sites between two adjacent oxygen planes are equivalent with respect to any uniaxial stress.

It is obvious that σ -sublattices are different from E-sublattices separated by an electric field, since, as it is verified in the figure 1, sites submitted to the same odd crystal field are on lines joining the fourth next-neighbours, like lines joining A and A', B and B'. Then an electric field parallel to the C_3 -axis distinguishes sites on an A-A' line from sites on a B-B' line. On the other hand it is noticed that the σ -sublattices are the same ones separated by a magnetic field [10].

From symmetry considerations, the crystal field components, which can induce shifts of the $E \rightarrow {}^4A_2$ transition or of the R_1 fluorescence line opposite for Cr^{3+} ions in the two different sublattices, would transform as the E representations of the trigonal group. In the t_2^3 configuration of the 2E states, the trigonal field induced by the environment of C_3 symmetry and the spin-orbit interaction have matrix elements equal to zero but between states of 2E and 2T_2 [11]. It is reminded that the splitting of 29 cm^{-1} between the $\bar{E}$ and $\bar{2A}$ levels comes from the combined effect of trigonal field and spin-orbit interaction. This splitting is slightly modified by configuration interaction [12].

After ${}^2E - {}^2T_2$ mixing by trigonal field and spin-orbit interaction, E and T_2 crystal fields induced, for instance, by uniaxial stress have only matrix elements between $\bar{E}$ states and $\bar{2A}$ states and none inside $\bar{E}$ or $\bar{2A}$ doublets. Therefore we expect that the effect of E crystal fields is quadratic by mixing $\bar{E}$ and $\bar{2A}$ states after ${}^2E - {}^2T_2$ mixing by trigonal field and spin-orbit interaction [13], or by direct ${}^2E - {}^2T_2$ mixing. Furthermore we notice that crystal fields transforming as E representation of trigonal group coming from E_g representation of O_h group have an effect on the energy at the sixth or fourth order of perturbation, whilst crystal fields transforming as E coming from T_2 have an effect on the energy at the fourth or second order respectively. Then we will only take into account the crystal fields transforming as $E(T_2)$ coming from T_2 .

Crystal field transforming as E is the sum of terms proportional to spherical harmonics of order 2 and of order -4 [12]. The variation of the first terms under stress is proportional to the local tensors α_{ik} given by [14] :

$$\alpha_{ik} = \sum_{st} G_{ikst} \sigma_{st} \quad (1)$$

and the variation of the second terms proportional to local tensors β_{iklm} :

$$\beta_{iklm} = \sum_{st} H_{iklmst} \sigma_{st} \quad (2)$$

where G_{ikst} and H_{iklmst} are functions of the macroscopic compliance tensor and of the 14 independent components of the internal strain tensor.

A complete theory of the uniaxial stress effect on optical transitions in corundum will be given in another paper [14].

Although the shift of the R_1 line ($\bar{E} \rightarrow {}^4A_2$) under stress coming from $E(T_2)$ strains is quadratic, it is possible to observe a splitting of the experimental line due to the separation of the Cr^{3+} ions in the two σ -sublattices. Actually, the non-diagonal elements are the sum of terms which have the same sign for the two sublattices and terms which have opposite sign in sublattice of type A and sublattice of type A' (Fig. 1).

Finally it is found, after determination of the different matrix elements of the ion-strain interaction operators and perturbation calculation, that the splitting δE , coming from the separation of Cr^{3+} ions into two different sublattices by a pressure P following an axis (θ, φ) in the referential (x_1, x_2, x_3) , is given by the following equation :

$$\delta E = CP^2 \cos \theta \sin^3 \theta \cos 3 \varphi . \quad (3)$$

The splitting δE would be maximum for a pressure along an axis in a plane of C_3 and C_2 axes at $\pi/3$ from the C_3 -axis.

Fig. 2. — R_1 fluorescence without and with two different applied pressures along a direction $\theta = 61 \pm 2^\circ$, $\varphi = 8 \pm 2^\circ$.

The major part of the effect expressed by the C constant is due to the interaction with the other t_2^3 levels, the ${}^2E(2A)$ contributing about a 83 % and the 3 levels issued from 2T_2 about 17 %.

The experimental set-up is the following. The ruby crystal is set in a pneumatic press which allows a uniaxial stress to be applied higher than 150 kp mm^{-2} on the crystal. The crystal dimensions are about $2 \times 2 \times 2.5 \text{ mm}$. The press is introduced in a cryostat and the ruby crystal is immersed in superfluid helium at 2 K. The fluorescence is excited at 580 nm in the ${}^4A_2 \rightarrow {}^4T_2$ band by a pulsed Rh 6G dye laser. The fluorescence is analysed by a Sopra 1.5 m monochromator, the dispersion and resolution of which are respectively $2.7 \text{ \AA/mm}$ and 120 000 at the second order. The ruby crystals supplied by C.G.E. (Marcoussis) were obtained by the Czochralsky method. The Cr^{3+} concentration was 0.06 at %. The orientation of the crystals was confirmed by X-ray diagram.

The R_1 fluorescence line is drawn in figure 2 without and with different pressures along a direction corresponding to $\theta = 61 \pm 2^\circ$ and $\varphi = 8 \pm 2^\circ$. These spectra under stress show the splitting of the two fluorescence lines separated by the 0.38 cm^{-1} splitting of the ground level. It is obvious that the splitting which appears with the applied pressure is due to the separation of Cr^{3+} ions in the two σ -sublattices, because the degeneracy of the different levels cannot be lifted by a crystal field from Kramers's theorem. In figure 2 we see that, when the splitting induced by the stress approaches 0.38 cm^{-1} , the two middle lines overlap completely.

Fig. 3. — Splitting δE as a function of the applied pressure $\theta = 61^\circ \pm 2^\circ$, $\varphi = 8^\circ \pm 2^\circ$.

Figure 3 shows that the splitting of R_1 line induced by uniaxial stress is quadratic as a function of the applied pressure. We have not represented the shift of the total R_1 fluorescence towards low energies. It has been measured by Feher and Sturge [2] and appears linear, at least for not very high pressures. This linear shift is principally due to the variation of the trigonal field [15].

Similar measurements have been performed for another direction of the applied pressure $\theta = 29 \pm 2^\circ$, $\varphi = 8 \pm 2^\circ$. At a pressure of 140 kp mm^{-2} the splitting δE is hardly measurable ($\delta E \sim 0.07 \text{ cm}^{-1}$). With this same pressure for the first direction ($\theta = 61 \pm 2^\circ$, $\varphi = 8 \pm 2^\circ$) $\delta E = 0.30 \text{ cm}^{-1}$. These relative values are in agreement with equation (3).

This experiment confirms the existence of two sublattices for the Cr^{3+} ions in ruby, the degeneracy of which is lifted by a uniaxial stress. In agreement with theory, the splitting which appears in the R_1 fluorescence is quadratic with the pressure. This work was carried out in connection with measurements of resonant and non-resonant energy transfers between the σ -sublattices [16].

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References

- [1] KAPLYANSKII, A. A., PRZHEVUSKII, A. K., *Phys. Status Solidi* **11** (1965) 629.
 - [2] FEHER, E., STURGE, M. D., *Phys. Rev.* **172** (1968) 244.
 - [3] LOUAT, R., LACROIX, R., DUVAL, E., CHAMPAGNON, B., *Phys. Status Solidi B* **69** (1975) 33.
 - [4] CHAMPAGNON, B., DUVAL, E., *J. Phys. C* **13** (1980) 131 ; **13** (1980) 141.
 - [5] DUVAL, E., LOUAT, R., CHAMPAGNON, B., LACROIX, R., WEBER, J., *J. Physique* **36** (1975) 559.
 - [6] CHAMPAGNON, B., DUVAL, E., LOUAT, R., *Phys. Status Solidi B* **69** (1975) 339.
 - [7] COUSINS, C. S. G., *J. Phys. C* **11** (1978) 4881 ; **14** (1981) 1585.
 - [8] LACROIX, R., DUVAL, E., CHAMPAGNON, B., *J. Phys. C* **15** (1982) 5945.
 - [9] BORN, M., HUANG, K., *Dynamical theory of crystal lattices* (Oxford : Clarendon) 1954.
 - [10] GESCHWIND, S., REMEIK, J. P., *Phys. Rev.* **122** (1961) 757.
 - [11] SUGANO, S., TANABE, Y., KAMIMURA, H., *Multiplets of transition — Metal ions in crystals* (Academic Press ; New York, London) 1970.
 - [12] SUGANO, S., PETER, M., *Phys. Rev.* **122** (1961) 381.
 - [13] BLUME, M., ORBACH, R., KIEL, A., GESCHWIND, S., *Phys. Rev. A* **139** (1965) 314.
 - [14] LACROIX, R., to be published.
 - [15] STEDMAN, G. E., *J. Chem. Phys.* **51** (1969) 4123.
 - [16] MONTEIL, A., DUVAL, E., ATTAR, A., VILIANI, G., to be published.
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