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## Vibronic contribution to the low temperature luminescence of $\text{KZnF}_3 : \text{Ni}$ . A quantitative approach

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**Résumé.** — Nous avons calculé la bande d'émission, à  $20\,000\text{ cm}^{-1}$ , dans  $\text{KZnF}_3 : \text{Ni}$  à 10,2 K en considérant les interactions multiphonons dans l'approximation du couplage linéaire. A partir de la densité d'états de phonon, un accord satisfaisant entre les courbes expérimentales et calculées a été obtenu en prenant le même facteur de couplage ( $S = 3,8$ ) pour tous les phonons.

**Abstract.** — The emission band at  $20 \times 10^3\text{ cm}^{-1}$  in  $\text{KZnF}_3 : \text{Ni}$  at  $T = 10.2\text{ K}$  is calculated as a summation of several phonon contributions within a linear coupling approximation. From the knowledge of the phonon density of states, a quite reasonable agreement with the experimental curve is obtained with just a single coupling parameter  $S = 3.8$ .

### 1. Introduction.

The search for solid-state laser sources has a special interest due to its quite broad potential applicability. From biology to communication problems a definite interest exists for stable or non-degradable coherent light sources. In the optical communication field, an emerging market plainly justifies a rush towards laser sources operating at frequencies falling within the optical fiber transmitting windows (1.3-1.6  $\mu\text{m}$ ).

Among these sources, fluorides or oxides doped with metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{V}^{2+}$ ) constitute a quite broad family. Some of these, as  $\text{KMnF}_3$ ,  $\text{KMgF}_3$  and  $\text{KZnF}_3$  not only fulfil the stability conditions but large size crystals with laser quality have already been grown [1].

The basic laser configuration developed by Kogelnik *et al.* [2], Mollenauer and Olsen [3] has been proven reasonably operational [4] for these systems.

The luminescence of  $\text{Ni}^{2+}$  ions at  $20 \times 10^3\text{ cm}^{-1}$  and  $13 \times 10^3\text{ cm}^{-1}$  in  $\text{MgO}$ ,  $\text{KMgF}_3$ ,  $\text{MgF}_2$  and  $\text{KZnF}_3$  has been correctly assigned by Vehse *et al.* [5] as due to  ${}^1\text{T}_{2g} \rightarrow {}^3\text{A}_{2g}$  and  ${}^1\text{T}_{2g} \rightarrow {}^3\text{T}_{2g}$  transitions respectively. The infra-red band has been qua-

litatively interpreted as a mixture of magnetic dipole and phonon assisted electric-dipole transitions whereas the symmetry forbidden electronic transition  ${}^1\text{T}_{2g} \rightarrow {}^3\text{A}_{2g}$  gives rise to a vibronic band due to phonon creation. This band is strongly temperature dependent; a proper interpretation requires the consideration of the impurity coupling with the phonon modes throughout the whole Brillouin zone of the crystal.

This work gives a contribution to the quantitative understanding of the phonon assisted  ${}^1\text{T}_{2g} \rightarrow {}^3\text{A}_{2g}$  luminescence in the  $\text{Ni}^{2+}$  doped fluoroperovskite prototype  $\text{KZnF}_3$  at low temperatures, where spectral details are pronounced. The importance of the phonon dispersion curves is stressed and through a simplified crystal to impurity coupling parameter, a theoretical result is obtained and compared with the experimental data. Possible improvements of the model are also underlined.

### 2. Sample preparation.

Most of the fluoroperovskites are characterized by a high instability in the liquid state that increases with the melt temperature of the various compounds. For this reason,  $\text{KCoF}_3$  and  $\text{KNiF}_3$  which melt respec-

(†) In memoriam.

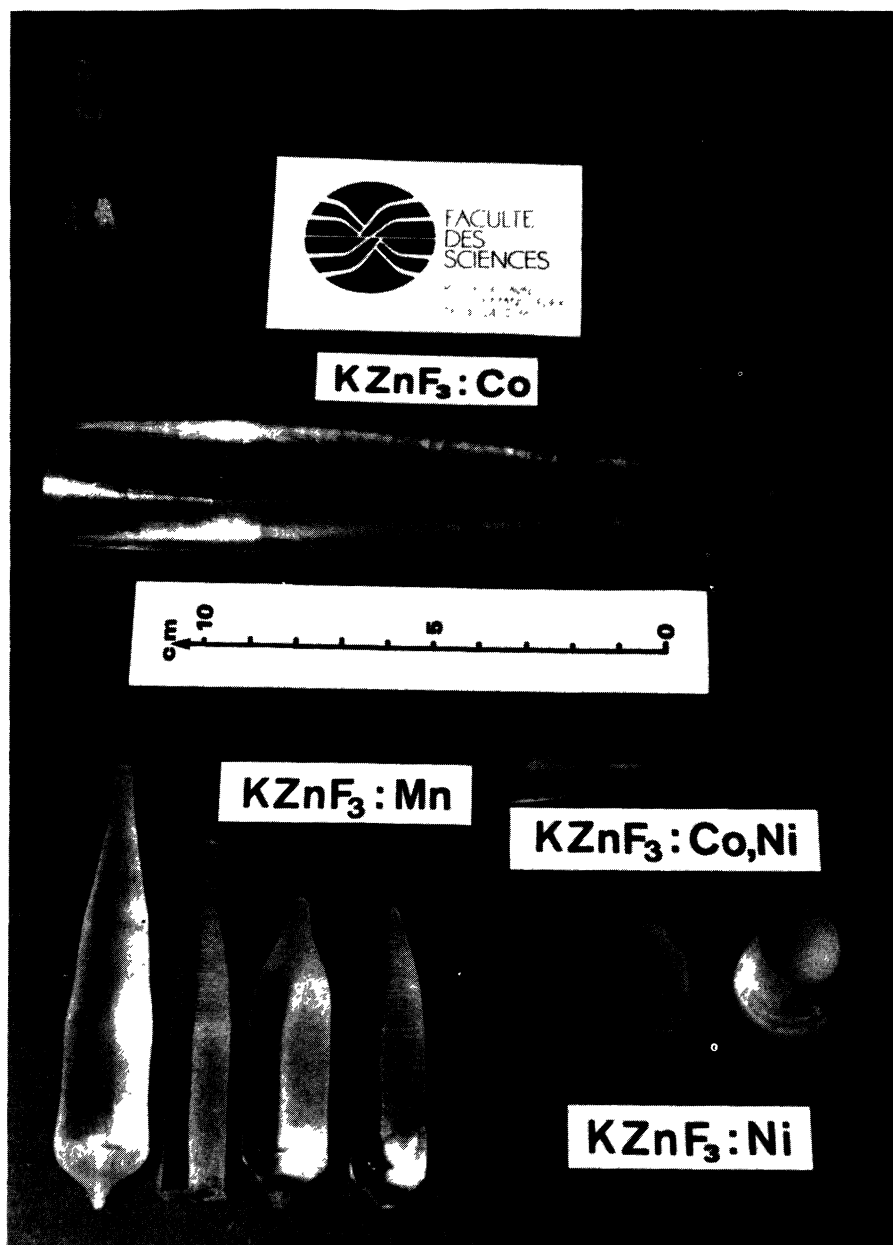


Fig. 1. — As-grown boules of  $\text{KZnF}_3$ ,  $\text{KZnF}_3 : \text{Ni}$ ,  $\text{KZnF}_3 : \text{Co}$  and  $\text{KZnF}_3 : \text{Mn}$ .

tively at 1 032 °C and 1 130 °C are found to be much more stable in a  $\text{KZnF}_3$  melt (870 °C) than in a  $\text{KMgF}_3$  melt (1 070 °C) [6]. The Czochralski growth of pure  $\text{KZnF}_3$  has been described in detail in an earlier paper [1]. For  $\text{KZnF}_3 : \text{Ni}$  pulling, the starting materials were repulled single crystals of  $\text{KZnF}_3$  and Bridgman-Stockbarger  $\text{KNiF}_3$  single crystals. Similarly, for  $\text{KZnF}_3 : \text{Co}$ , repulled single crystals of  $\text{KZnF}_3$  and Bridgman-Stockbarger  $\text{KCoF}_3$  single crystals were used.

All the Czochralski growth runs of doped crystals were performed using [100] seeds in a 100 mm diameter vitreous carbone crucible. The pulling and rotation speeds were respectively 10 mm/h and 15 rpm, and no automatic control for the diameter was used.

Typically, single crystal boules of 50 cm<sup>3</sup> were grown from melts containing between 0.1 and 1 % of dopant materials. All of them were optically clear, free of visible inhomogeneities and none of them cracked even without an annealing process. Figure 1 shows the as-grown boules of  $\text{KZnF}_3$ ,  $\text{KZnF}_3 : \text{Ni}$ ,  $\text{KZnF}_3 : \text{Co}$  and  $\text{KZnF}_3 : \text{Mn}$ .

A chemical analysis done by atomic absorption technique has shown that no significant radial gradient of doping impurities is observed for all crystals. However, to obtain long rods with an homogenous dopant concentration, that is to say, with variations less than 10 % in 100 mm, the melt volume has to be larger than ten times the boule volume.

For samples of  $\text{KZnF}_3 : \text{Co}$  it was found [7] that

the doping concentration can increase with no decrease in the luminescent quantum yield. Consequently, crystal pulling runs of  $KZnF_3$  doped with more than 1 % of nickel or cobalt are in progress in our laboratory. --

**3. Experiment.**

The emission spectra were excited with a Spectra-Physics 165 argon ion laser and the emitted light was collected at 90° and dispersed with a Spex double-monochromator. Detection was done with a cooled S-11 reponse ITT photomultiplier tube and conventional analogic amplification. An air-Products closed-cycle cryogenerator was used for the low temperatures.

In order to avoid clustering effects in the spectra, a single crystal of  $KZnF_3$  was chosen containing only 10 ppm of nickel. As shown in figure 2, at room temperature, a continuous bell-shaped emission band is observed. The anti-stokes luminescence provides a remarkable evidence of vibronic effects. Though this luminescence band has a simple spectral shape at room temperature, several phonon levels are in interplay both at the excited and the ground state electronic levels. The spectrum smoothing is a conse-

quence of this complicated emission. A low temperature spectrum (10.2 K) was chosen as a departure point in order to have good vibrational details and a simpler phonon set of levels.

At low temperatures, thermally excited phonons are completely negligible and, consequently, any anti-Stokes lines turns out to be quite weak. Therefore, in order to excite the crystal, a frequency well above the emission band must be used. The 4 765 Å line was then chosen as a pump line due to its coincidence with one of the crystal's absorption bands (Fig. 3).

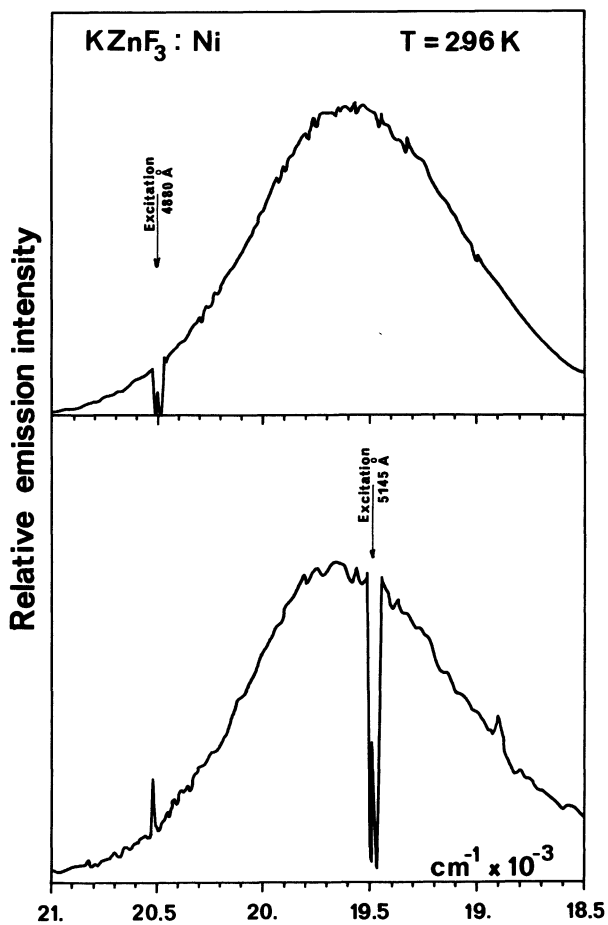


Fig. 2. — Luminescence emission at room temperature under 4 880 Å and 5 145 Å excitations, respectively.

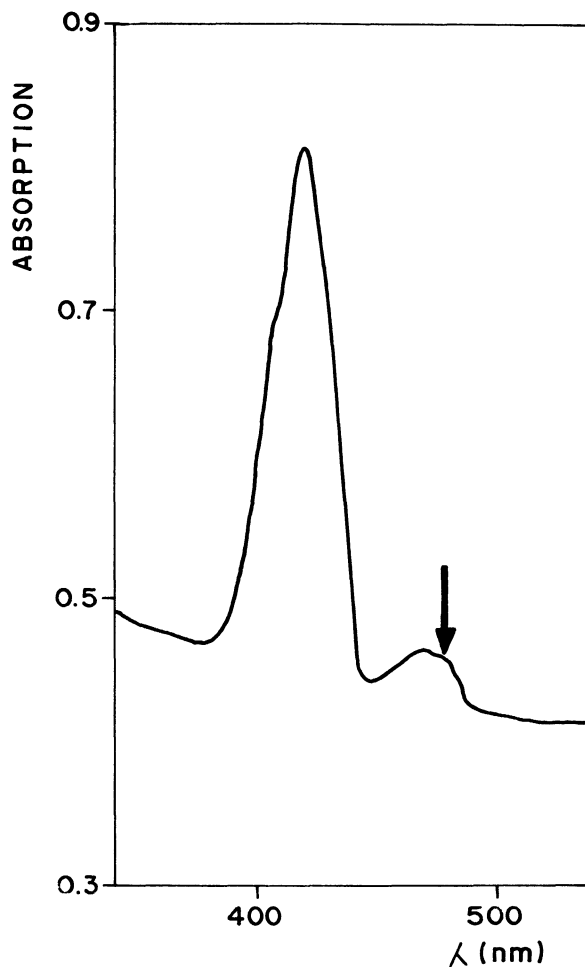


Fig. 3. — Room temperature absorption for  $KZnF_3 : Ni^{2+}$ . The 4 765 Å laser line is indicated by an arrow.

A typical emission spectrum at low temperature ( $T = 10.2$  K) is shown in figure 6. According to Vehse *et al.* [5] the magnetic dipole  $^1T_{2g} \rightarrow ^3A_{2g}$  origin presumably lies midway between the first well defined Stokes line and its barely seen anti-Stokes counterpart.

**4. Model and results.**

We have chosen to work with Pryce's model [8], that assumes a linear coupling with an arbitrary

phonon spectrum. For the present calculation no impurity localized modes are considered but just the fact the impurity plays the role of connecting the phonons to the luminescent yield through the translational symmetry breaking it produces in the crystal structure. The localized character of this impurity makes the involved wavevectors completely unspecified, i.e., the whole Brillouin zone modes could manifest themselves in the luminescence spectra. The  $O_h$  symmetry at the impurity site sets its restriction on what modes are allowed in the electric-dipole transitions leading to the luminescence spectrum. These modes can be calculated, in principle, for specific points in the Brillouin zone. However, if one takes a single phonon branch in the wavevector space, its symmetry varies from point to point making a general symmetry assignment quite difficult for computational purposes. Assuming a linear coupling, only a change in the configurational coordinates without any change in the curvature of the harmonic potentials is considered [8]. Then, for a given mode of frequency  $\omega_\alpha$ , the dimensionless coupling constant  $S_\alpha$  is classically defined as

$$S_\alpha \hbar \omega_\alpha = \frac{1}{2} K_\alpha Q_{0\alpha}^2 \quad (1)$$

where  $Q_{0\alpha}$  is the change in equilibrium coordinates between the two electronic states and  $K_\alpha$  represents the curvature of the harmonic potential. These complex problems are then simplified by considering all modes as active in the luminescence spectra and taking a simple coupling constant  $S$  for all of them.

The emitted spectrum is denoted as

$$I(h\nu) = \frac{64 \pi^4 \nu^4}{3 c^3} G(h\nu) \quad (2)$$

$G(h\nu)$  being the normalized spectral function.

Pryce [8] shows that  $G(h\nu)$  can be developed as a summation of phonon spectral shapes  $B_p(h\nu)$  as

$$G(h\nu) = \sum_{p=1}^{\infty} W_p B_p(h\nu) \quad (3)$$

where  $W_p$  are proper weights corresponding to Poisson's distribution around the average number  $S$  of created phonons, i.e.,

$$W_p = e^{-S} \frac{S^p}{p!} \quad (4)$$

$B_p(h\nu)$  describes a specific shape contribution where  $p$  phonons are involved and it is normalized as

$$\int_0^\infty B_p(h\nu) d(h\nu) = 1.$$

The lowest order normalized shape is given by [8]

$$B_1(h\nu) = \frac{\rho(\hbar\omega)}{\int \rho(\hbar\omega) d(\hbar\omega)} \quad (5)$$

where  $\rho(\hbar\omega)$  represents the phonon density of states. From now on, a normalized phonon density of states will be assumed.

$B_2(h\nu)$  would represent processes where two different phonons  $\alpha$  and  $\alpha'$  are created and is given by

$$B_2(h\nu) = \int_0^\infty \rho(h\nu + \hbar\omega') \rho(\hbar\omega') d(\hbar\omega'). \quad (6)$$

A further simplification can be done for the higher order shapes. As the number of phonons increases, the number of possible frequency combinations is quite large, it should be reasonable to suppose that the probabilistic central limit theorem would apply; then, for  $p \geq 3$ ,  $B_p$  can be approached by a Gaussian shape of width  $\sigma$  around the average  $p\bar{\hbar\omega}$

$$B_p(h\nu) \cong \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{(h\nu - p\bar{\hbar\omega})^2}{2\sigma^2}\right) \quad (7)$$

where,

$$\bar{\hbar\omega} = \int_0^\infty \hbar\omega \rho(\hbar\omega) d(\hbar\omega).$$

The  $S$  factor does not influence the shape of the first and second order contributions but only their relative weight. Thus, the width  $\sigma = \sqrt{p}\sigma_0$  can be estimated, with any value of  $S$ , from the  $B_2$  contribution as  $\sqrt{2}\sigma_0$ . In this way, if one knows the phonon density of states, the whole spectrum can be generated in a simplified way with only  $S$  as a parameter.

The phonon density of states  $\rho(\hbar\omega)$  was calculated from the rigid ion model previously established for  $\text{KZnF}_3$  [9]. We have solved the eigenvalues of the dynamical matrix at  $1.25 \times 10^5$  points forming a uniform mesh in the first Brillouin zone. By sampling the eigenfrequencies in steps of  $1 \text{ cm}^{-1}$  we obtained the histogram of the phonon density of states presented in figure 4.

Figure 5 shows the first, second and higher order contributions to the spectrum. From the second order contribution the width  $\sigma_0$  is estimated to as  $\sigma_0 = 100 \text{ cm}^{-1}$ . Figure 6 compares the experimental emission spectrum with the one calculated with  $S = 3.8$ .

## 5. Conclusions.

Within the adopted model it is quite remarkable that even with the strong simplifications made, a reasonable agreement was obtained between the experimental and the calculated luminescence. The reliable value obtained for the coupling constant  $S = 3.8$  is in agreement with the estimate  $S \sim 4$  done by Kunzel *et al.* [4] for  $\text{KZnF}_3 : \text{Co}^{2+}$ . This agreement should be expected as nickel and cobalt have very similar radii.

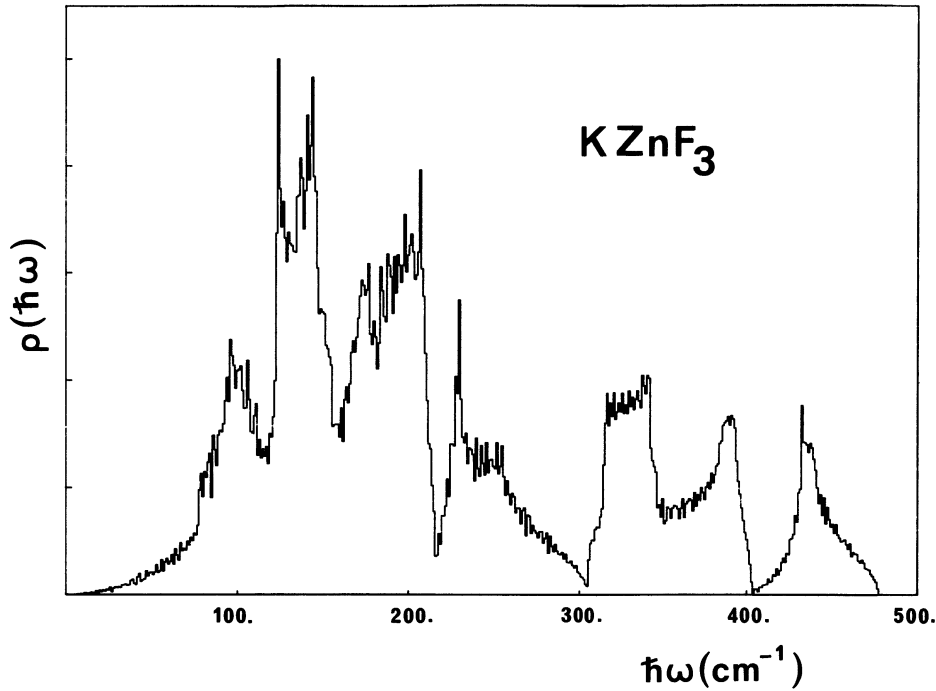


Fig. 4. — Histogram of the phonon density of states  $\rho(\hbar\omega)$  for  $\text{KZnF}_3$ , calculated with a rigid ion model.

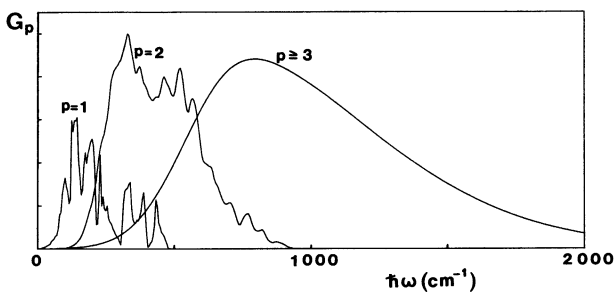


Fig. 5. — First, second and higher order contributions to the spectrum.  $S = 3.8$ ,  $\sigma_0 = 100 \text{ cm}^{-1}$ .

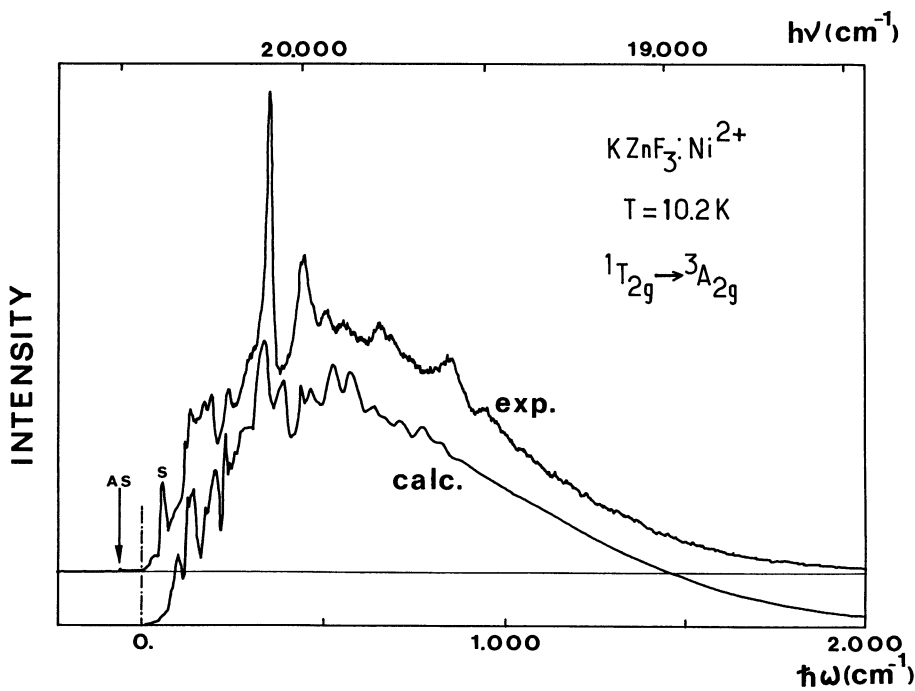


Fig. 6. — Experimental and calculated curves at  $T = 10.2 \text{ K}$ ,  $S = 3.8$ ,  $\sigma_0 = 100 \text{ cm}^{-1}$ . Calculated curve corrected for the S-11 photomultiplier response.

Before proceeding to a more sophisticated model with different electron-phonon couplings and considering the correct electric-dipole transitions, one has to consider several other possible improvements. Among these, one could observe that small displacements in some of the phonon frequencies might produce a quite large change in amplitudes whenever two lines come very close in frequency. This could be done through a refinement of the phonon density of states by replacing the rigid ion model by a shell model.

Another step should include a study of the tempe-

rature evolution of this luminescence taking into account all of the necessary phonon excited states.

In  $\text{KZnF}_3 : \text{Ni}^{2+}$  a reasonable strong coupling exists due to the tightness of the unit cell for the Ni ion. One could expect that a much weaker coupling should exist in  $\text{CsCaF}_3 : \text{Ni}^{2+}$ , that has a larger unit cell. Therefore, a more structured spectrum should be expected for this crystal.

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