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The fine structure and the origin of the 0.84 eV no-phonon luminescence in GaAs : Cr

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Résumé. — Nous avons effectué des expériences de spectroscopie à haute résolution sur la luminescence à 0,84 eV émise par GaAs : Cr. Nous obtenons un nouveau schéma des niveaux d'énergie. Ce schéma ainsi que les forces d'oscillateur sont bien interprétés en considérant l'émission par l'ion Cr^{2+} en site Ga soumis à une perturbation de symétrie C_{3v} .

Abstract. — We have performed high resolution luminescence spectroscopy of a chromium related no-phonon multiplet. We deduce a new level scheme. This scheme and the oscillator strengths are conveniently interpreted as arising from transitions at substitutional Cr^{2+} ions on a Ga-site subjected to a perturbation of C_{3v} symmetry.

1. Introduction. — A sharp no-phonon line at 0.84 eV with an accompanying multiphonon sideband at a lower energy has been attributed to an internal transition ($^5\text{E}-^5\text{T}_2$) of the Cr^{2+} ion on a substitutional Ga-site by Koschel *et al.*, 1976 and Stocker *et al.*, 1976 [1].

Clerjaud *et al.* [2] have recently observed an absorption line at 0.825 eV and interpreted it, in agreement with E.P.R. results, as the $^5\text{B}_2-^5\text{A}_1$ transition at Cr^{2+} on a substitutional Ga-site.

White *et al.* [3] and Picoli *et al.* [4] have proposed alternative models for the 0.84 eV no-phonon system.

A few days ago, we were informed of Zeeman experiments by B. C. Cavenett *et al.* and Eaves *et al.* on the 0.84 eV luminescence in GaAs : Cr which suggest a [111] symmetry axis for the associated centre [5].

The fine splitting of the no-phonon luminescence spectra occurring near 0.839 eV in GaAs : Cr has gained attention since the observation of E. C. Lightowers *et al.* (L.H.P.) [6]. The precise nature of this splitting and the associated level scheme are of paramount importance for the assignment of the transitions.

We have performed high resolution luminescence spectroscopy on this chromium related, no-phonon multiplet. The semi-insulating bulk materials were

obtained from different sources : the fine structure appears to be remarkably constant while the total intensity is strongly crystal dependent. At the lowest temperatures the sample is immersed in liquid He. The luminescence is excited by the 752.5 nm krypton laser line, dispersed by a Spex 1404 monochromator with a 600 grooves per mm grating blazed at 1 μm , and detected by a Northcoast Ge detector.

We deduce the new level scheme and give the model for the defect.

2. The experiment. — Figure 1 shows two spectra recorded at 3 K and 9 K respectively. Compared to the L.H.P. study this work is characterized by improved sensitivity, and spectroscopic resolution (0.03 meV). Also, we can work at lower temperatures. We find that the F line is now very well separated from G, the E and H lines are really doublets and the I and J lines are broader than others for the lowest temperatures. Our measurement of the G linewidth (FWHM) gives 0.07 meV.

Very accurate thermal activation measurements of the intensities of the lines give an identical behaviour for (i) the E and C lines (precision 4 %), (ii) the B, B' and D' lines (precision 4 %), and (iii) the A' and A'' lines (precision 7 %). This shows that the E, and C lines arise from the same initial excited level; the same conclusion is true for B, B', D' and for A', A'' respectively.

The measured thermal activation energies differ

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Fig. 1. — Photoluminescence spectra of the 0.839 eV no-phonon structure obtained from semi-insulating GaAs : Cr.

from those expected from the energy levels positions and thus reveals that the thermalization on the excited states is not achieved.

We are now able to give a convenient energy level scheme with the assignment of the transitions (Fig. 2). For each line, the position of the initial state agrees completely with our luminescence thermal activation analysis while we are helped for the choice of the final state by the L.H.P. thermal activation absorption measurements [6]. We see that this scheme differs very much from the L.H.P. proposition, but we emphasize that the spectral position of the lines and the thermal activation measurements in luminescence (our results) and absorption (L.H.P. data) can be fitted only with this arrangement of levels. In the L.H.P. scheme the ground level system was not in good agreement with the measured activation

Fig. 2. — On the left : The energy level scheme deduced from near infrared optical spectroscopy. On the right : The energy level scheme at zero magnetic field deduced from E.P.R. experiments [9]. The dotted arrows which join the 5T_2 levels shows the expected evolution toward the static limit. (Γ_n denotes a representation of T_d).

energies, while the positioning of the D line did not agree with the spectral position.

We observe that I and J lines are much broader than other lines at low temperatures. Also their final state is clearly separated from others ground states. For these reasons we believe that I and J do not correspond to pure no-phonon transitions but their final state (dashed lines on figure 2) originate from excited vibrational states depressed in energy. So we propose therefore to omit the dashed levels on figure 2 from the pure no-phonon level scheme.

3. The model for Cr^{2+} ($3d^4$) in T_d symmetry. — At a site of tetrahedral symmetry, the lowest free ion term 5D of $Cr^{2+}(3d^4)$ is splitted by the crystal-line field into a lower orbital triplet 5T_2 and a higher orbital doublet 5E . Important features of the new level scheme may be interpreted if we consider the 5E - 5T_2 transitions. The analysis follows closely the procedure introduced by G. A. Slack *et al.* [8] in order to explain the absorption spectra of tetrahedral $Fe^{2+}(3d^6)$ in cubic ZnS, CdTe and $MgAl_2O_4$. Only some adaptations are necessary, so we give here the main results obtained for our case.

(i) The six lowest levels are described by the effective hamiltonian :

$$\mathcal{H} = \zeta(\mathbf{L} \cdot \mathbf{S}) + \mu(\mathbf{L} \cdot \mathbf{S})^2 + \rho(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2) \quad (1)$$

in which $l = 1$ and $S = 2$.

The experimental positioning of levels is fitted for :

$$\zeta = -0.06 \text{ meV}; \quad \mu = -0.03 \text{ meV}; \quad \rho = 0.17 \text{ meV}.$$

This description assumes a dominant strong dynamic Jahn-Teller (J-T), $T \otimes e$ coupling and a weak spin-orbit splitting. The J-T energy E_{JT} may be deduced by taking $\lambda \simeq 7.4 \text{ meV}$ (the free ion value of the spin-orbit parameter), $\hbar\omega \simeq 8.7 \text{ meV}$ (the energy of the involved phonon) so that $E_{JT} \simeq 28 \text{ meV}$ from Ham's formula

$$\left(\zeta \simeq \lambda \exp - \frac{3 E_{JT}}{2 \hbar \omega} \right).$$

The ordering of levels according to increasing values of the energy is : 0 meV (Γ_1); 0.18 meV (Γ_4^-); 0.28 meV (Γ_3); 0.61 meV (Γ_5^-); 0.68 meV (Γ_4^+); 0.82 meV (Γ_5^+); (the notation Γ_n^+ or Γ_n^- enables us to distinguish between different Γ_n levels). The T_d labels Γ_n are given on figure 2.

(ii) The five upper levels result from the second order spin-orbit splitting of the tetrahedral 5E states (a weak J-T, $E \otimes e$ coupling cannot disturb the spacing very much [8]). The ordering of levels according to increasing values of the energy is 0 meV (Γ_2); 0.98 meV (Γ_5); 1.54 meV (Γ_3); 2.41 meV (Γ_4); 2.70 meV (Γ_1). We notice that the equal-

spacing is not well satisfied which suggests some deficiencies in the model.

(iii) The two vibronic levels located just above the set of the six ground no-phonon levels may be interpreted as follows. F. S. Ham *et al.* [7] have shown that an important depression in energy of the first excited vibronic levels can occur when the energy of the involved phonon is not very much larger than the spin-orbit parameter of the free ion. This appears to be the situation here.

Such a model offers two main kinds of discrepancies with the experiments :

(i) The equal-spacing between the 5E levels is not well observed which suggest that some *perturbation interaction* has not been considered.

(ii) If the observed (AA' CDD' EE' HG) lines correspond to electric-dipole transitions allowed by group theory we see other lines (A' BB' FH') which are forbidden while we cannot observe some others ($\Gamma_3 \rightarrow \Gamma_4^-$, $\Gamma_4 \rightarrow \Gamma_4^+$, $\Gamma_4 \rightarrow \Gamma_5^-$) which are allowed.

Furthermore it appears very clearly that the E.P.R. description [9] and our *near infrared description* of the Cr^{2+} ground states are not identical. However, we see on figure 2 that the six 5T_2 levels are grouped according to the eigenvalues of S_z (or S_x , S_y) as they must be in the static limit : then the states belonging to $\Gamma_1 + \Gamma_3 + \Gamma_4^-$, $\Gamma_4^+ + \Gamma_5^-$, Γ_5^+ , correspond respectively to the eigenvalues ± 2 , ± 1 , 0. (The reader should note that three quantization axes are involved in this discussion.) Near this limit the degeneracies are lifted by interactions between the three wells of the adiabatic potential surfaces. The comparison with the E.P.R. level scheme (Fig. 2) shows that the two descriptions are similar ; for example, $-\rho$ and the so-called $D(^5T_2)$ parameter, which are equal in the static limit, are not much different (we find $-\rho = -0.17$ meV while Krebs *et al.* [9] gives $D = -0.23$ meV).

4. The consequences of a C_{3v} perturbation. — We suggest now that the above so-called *perturbation interaction* has a C_{3v} symmetry (for instance, one impurity atom is present in the neighbourhood in the [111] direction). So the *E.P.R. centre* and the present 0.84 eV *centre* are identical excepted for this presence. The main consequences are the following :

(i) Such a perturbation is strongly quenched by the J-T $T \otimes e$ coupling which affects the 5T_2 states [10]. (The C_{3v} coupling is assumed smaller than the J-T coupling because the reverse situation would not give

a convenient description of the set of ground levels.) We have really studied the case of a C_{3v} interaction added to the effective hamiltonian (1) : the splitting generally gives ten levels (or seven if $\zeta = \mu = 0$) and no satisfying agreement with the experimental scheme can be obtained. It seems to us better, therefore, to consider the C_{3v} perturbation completely quenched and to maintain the description of the 5T_2 splitting as given by (1). Nevertheless, the small differences noticed above between the *E.P.R. centre* and the 0.84 eV *centre* ground states must be attributed to the different Cr^{2+} ion neighbourhoods.

(ii) W. Low *et al.* [11] have given the crystal-field treatment when no J-T coupling affects the system. When the spin-orbit coupling (λ) is larger than the C_{3v} perturbation (b_2) we get seven levels while for the reverse case we have five equally spaced levels (smaller splitting are neglected ; the spacing is

$$\frac{4 b_2 \lambda}{\Delta}, \quad \text{with } \Delta = 10 |Dq|,$$

Dq being the one electron cubic field parameter).

From symmetry considerations only, C. A. Bates *et al.* [12] deduced the most general hamiltonian describing the effects of spin-orbit coupling, trigonal field and J-T interaction within the 5E states of a $3d^4$ ion in a cubic system. The problem is then to obtain the values for the parameters which account satisfactorily for the experimental data : in this way we have no difficulty to fit the experimental arrangement of levels.

(iii) The C_{3v} interaction modifies entirely the selection rules for electric dipole transitions between the sets of the excited and ground levels. According to group theory, all the transitions are now allowed but the oscillator strengths are strongly dependent of the spin part of the quantum states. However a complete calculation is still necessary.

5. Conclusion. — We have obtained a convenient level scheme for the 0.84 eV no-phonon luminescence in GaAs : Cr. We interpret it as arising from a $\text{Cr}^{2+}(3d^4)$ ion on a substitutional Ga-site subjected to a C_{3v} perturbation. The model explains the important similarities as well as the differences between this centre and Cr^{2+} on a Ga-site in a perfect crystal.

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