Classification
Physics Abstracts
78.50 — 78.55

Evidence for energy transfer induced by superexchange in $\text{LaF}_3 : \text{Pr}^{3+}$

J. C. Vial and R. Buisson

Laboratoire de Spectrométrie Physique (*), B.P. 53 X, 38041 Grenoble Cedex, France

(Reçu le 15 juin 1982, révisé le 2 septembre, accepté le 10 septembre 1982)

Résumé. — Les taux d'extinction pour plusieurs paires de Pr^{3+} dans LaF_3 faiblement dopé ont été mesurés directement. Puisqu'ils sont significatifs pour quelques paires seulement, le mécanisme est à courte portée. A partir des valeurs mesurées, la forme du déclin de la fluorescence de cristaux fortement dopés est prévue. Le bon accord avec l'expérience montre l'intérêt de relier les mesures microscopiques et macroscopiques. Enfin, des arguments sont avancés pour prouver que le mécanisme de transfert est le superéchange.

Abstract. — Direct measurement of fluorescence quenching rates for various Pr^{3+} pairs in weakly doped LaF_3 are reported. Since few pairs only are quenched, the transfer mechanism is short range. From the rate values, the shape of the fluorescence decay for heavily doped samples is predicted. The good agreement with the observed decay proves the interest of the connection between microscopic and macroscopic measurements. Finally arguments are developed to prove that the transfer mechanism is superexchange.

Among the possible interaction mechanisms for optical excitation, exchange is often discounted in rare earth inorganic systems although Birgeneau pointed out that it could be as efficient as the other mechanisms [1]. Frequently, a multipolar electric interaction is postulated, the nature of which is deduced from the shape of the donor fluorescence decay using the Inokuti-Hirayama formula [2]. When used for randomly doped crystals, that method implies a statistical average over the possible positions of the acceptors around the donors and is subject to the hypothesis that a single mechanism is active. It is well known that the conclusions deduced from this « macroscopic » approach are questionable, the fit between theoretical and experimental decay curves never being perfect. Improvements of this approach either by Dornauf and Heber [3] and Siebold

(*) Laboratoire associé au C.N.R.S.

and Heber [4] with a « discrete model » instead of a continuous model, or by Hegarty *et al.* [5] who deduce the microscopic transfer rate between two nearby ions from macroscopic results, need nevertheless the hypothesis that a single mechanism is active.

It has been shown recently that microscopic transfer rates can be measured directly when a class of pairs of ions can be selectively excited [6]. Using weakly doped crystals, pairs are well « isolated » and their intrinsic behaviour is observed. From these measurements, it was inferred that the transfer mechanism could not be the same for weakly and strongly coupled pairs. The possible co-existence of various mechanisms has been considered by Watts [7] who showed, by numerical calculation of the quadrupole-quadrupole and dipole-dipole coupling strength between Yb^{3+} and Er^{3+} , that the former dominates the latter for ions separated by less than $9 \text{ \AA}$.

The results reported here, again based on the direct study of the properties of pairs, show unambiguously that a short range interaction dominates the dipole-dipole interaction and is responsible for the quenching previously attributed to dipole-dipole coupling from macroscopic measurements [8]. They are then used to predict, with success, the behaviour of more heavily doped samples : starting from microscopic values macroscopic experiments are explained.

The system studied, $\text{LaF}_3 : \text{Pr}^{3+}$, is a very well known system whose energy levels have been tabulated in detail by Carnall *et al.* [9]. Most of the energy transfer experiments made with it have been presented and analysed by Yen in a review paper on energy transfer in rare earth ions in crystals [10].

The present paper is centred on the quenching of the $^3\text{P}_0$ fluorescence. The first study of this quenching by Brown *et al.* [11] has shown that it results from cross relaxation between one Pr^{3+} excited and one nearby unexcited Pr^{3+} . This quenching has recently been studied by the Madison group with modern experimental techniques. Lai *et al.* [12], by a cooperative absorption, excite two neighbouring Pr^{3+} ions in PrF_3 with a single photon, putting one ion into the $^3\text{P}_0$ state, the other into the $^3\text{F}_2$ state. Ions excited into $^3\text{P}_0$ have then one less quenching channel, the nearby ions excited into $^3\text{F}_2$ being not able to cross relax with them. By measuring the change of the lifetime of these ions with respect to that of normally excited ions, the cross relaxation rate between two neighbouring ions is deduced. Hegarty *et al.* [8], using Inokuti and Hirayama formula, deduce also the value for this rate within the hypothesis of dipole-dipole coupling. To reach this conclusion, they must subtract from the fluorescence signal an exponential component they attribute to ions in « non quenching sites ».

In this work the values of the cross relaxation transfer rates responsible for the quenching of $^3\text{P}_0$ fluorescence are directly measured for various pairs after their selective excitation. They are then used to show that the interaction has a short range and to predict the quenching for more heavily doped crystals. The fact that these measurements are made with a 0.1 % doped crystal in which there is no macroscopic quenching (the main line, due to isolated ions has a long lifetime) is not a paradox but shows the peculiarity of the method.

1. Experimental results. — Figure 1 shows the absorption spectrum around the main $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition. It is now well established that satellites are due to pairs of ions [6]. By monitoring the fluorescence induced by a narrow dye-laser pulse, it is possible to record time resolved excitation spectra as shown in figure 1 or to observe the fluorescence decay after a selective excitation of a given satellite as given in figure 2. For the f line, the slow component associated with the central line has been subtracted from the actual signal. The decay for lines a and f is exponential for more than two decades, indicating that all the pairs associated with one line have the same dynamical properties. Values of the decay times τ are given in table I. It has not been possible, for lines c, d, e, to subtract the contribution of the wing of the central line because the decay times are too close. However, since the decay time in wings of the main line is shorter than that of lines c and d (this is deduced from the comparison of the two excitation spectra shown in figure 2), its measurement gives an upper limit for lines c and d. This limit is given in table I.

Fig. 1. — The lower curve is the absorption spectrum of a $\text{LaF}_3 : 0.1\% \text{Pr}^{3+}$ sample around the $^3\text{H}_4 \rightarrow ^3\text{P}_0$ transition. The two other curves are time resolved excitation spectra of the $^3\text{P}_0$ fluorescence with two different delays after the laser pulse. Note that the gain for the $40\ \mu\text{s}$ spectrum is twice that for the $5\ \mu\text{s}$ spectrum.

The reduction of the decay time in the wing of the main line, already pointed out for heavily doped samples [13] as well for $^1\text{D}_2$ fluorescence in weakly doped samples [14] will be discussed elsewhere.

As first proposed by Brown *et al.* [11], the reduction of the $^3\text{P}_0$ lifetime results from a cross relaxation between an excited and an unexcited ion. From the measured lifetimes τ and the radiative lifetime $\tau_0 = 48 \times 10^{-6}\ \mu\text{s}$ of the isolated ions [15] it is easy to calculate the cross relaxation rate w_c for each satellite by

$$w_c = \frac{1}{\tau} - \frac{1}{\tau_0}.$$

The choice of τ_0 as the radiative lifetime for the ions of the pairs is justified by the fact that the relative intensities of the fluorescence lines corresponding to the transitions from $^3\text{P}_0$ towards the levels of the sublying multiplets are the same whether the central line or a satellite is excited. If the perturbation created on a Pr^{3+} by another nearby Pr^{3+} changed significantly the oscillator strengths of the transitions, it would be surprising that this change would be the same for all the transitions.

These results are now used to determine the nature of the coupling responsible for the observed cross relaxation. As it will appear below, this determination will result from strongly convergent evidence. The only remaining problem lies in the difficulty of associating a definite class of pairs with each satellite. This problem has already been pointed out [6] and its resolution would need uniaxial stress experiments as those made in ruby [16].

Fig. 2. — 3P_0 decay of a $\text{LaF}_3 : 0.1\% \text{Pr}^{3+}$ sample following a selective excitation : ■ of line f, ● of line a, ▼ of lines c, d, and the central line. The two other curves correspond to lines b and e. Note that for f line, the contribution of the wing of the main line has been subtracted.

Table I. — Values of the decay time τ and of the cross relaxation rate W_c for the various pairs associated with the satellite of figure 1.

Line	τ (μs)	W_c (μs^{-1})
a	22	2.5×10^{-2}
b	45.5	1×10^{-3}
c	> 47	$< 5.4 \times 10^{-4}$
d	> 47	$< 5.4 \times 10^{-4}$
e	~ 46.5	$\sim 5.4 \times 10^{-4}$
f	8.5	9.7×10^{-2}

The determination of the nature of the coupling between the two Pr^{3+} ions of a pair is based on three arguments now explained in detail.

1.1 VARIATION OF THE TRANSFER RATE WITH THE DISTANCE. — The sequence of the transfer rates of table I, after normalization is 1-0.26-0.01-0.006. From the LaF_3 structure [17], the possible pairs can be characterized by the couple $(n-R)$ when n is the number of sites at a given distance R from a La site. The list of these couples, starting from the lowest R , is

$$[(4-4.10), (2-4.25)], [(2-4.30), (4-4.42)], [(4-6.00), (2-6.14)] \dots \quad (1)$$

Pairs in the same bracket are nearly equivalent but those belonging to classes having $n = 2$ have a symmetry operator which inter-changes the two ions. This operator is a two-fold axis for the first and the third bracket, an inversion centre for the second bracket. If a dipole-dipole

mechanism is supposed for the cross relaxation, the rates would vary along the R^{-6} following normalized sequence : 1-0.81-0.75-0.64-0.10-0.089 and if a dipole-quadrupole transfer mechanism is supposed, the sequence would be R^{-8} i.e. : 1-0.75-0.68-0.55-0.048-0.040. Even if a satellite would correspond to more than one class of pairs, it is clear that these two sequences are incompatible with the sequence of the observed rates. This is the first argument for rejection of dipole-dipole and dipole-quadrupole mechanism.

1.2 ORDER OF MAGNITUDE. — From the energy levels of $\text{LaF}_3:\text{Pr}^{3+}$ [9], the more probable quenching processes for the $^3\text{P}_0$ fluorescence are :

$$|^3\text{P}_0, ^3\text{H}_4(1)\rangle \rightarrow |^1\text{G}_4(8), ^1\text{G}_4(9)\rangle \quad \text{and} \quad |^3\text{P}_0, ^3\text{H}_4(1)\rangle \rightarrow |^1\text{G}_4(9), ^1\text{G}_4(9)\rangle,$$

the former being assisted by the emission of an energy of 265 cm^{-1} as phonons, the latter needing the absorption of a phonon of 71 cm^{-1} . At low temperature, only the former is active. From the general theory developed by Holstein *et al.* [18] it is easy to show that the transfer rate takes the form

$$W = \frac{|\langle I | H_c | i \rangle|^2}{(E_i - E_f)^2} \cdot \left| \frac{2\pi}{h} |\langle v_i | H_{\text{OL}} | v_f \rangle|^2 \rho(E_f) \right| \quad (2)$$

where

$$|I\rangle = |^3\text{P}_0, ^3\text{H}_4(1)\rangle, \quad |F\rangle = |^1\text{G}_4(8), ^1\text{G}_4(9)\rangle$$

and $|i\rangle = |^1\text{G}_4(9), ^1\text{G}_4(9)\rangle$ the single intermediate state which, by far, gives the greatest contribution, E_i, E_f, E_l the energy of these electronic states, $|v_i\rangle$ and $|v_f\rangle$ the vibronic states associated with $|i\rangle$ and $|F\rangle$, $\rho(E_f)$ the density of states of the final state and H_{OL} an ion lattice Hamiltonian. Due to the fact that $\hbar\omega_D \sim 250\text{ cm}^{-1}$, two phonons of total energy of 265 cm^{-1} must be emitted between $|I\rangle$ and $|F\rangle$. Thus H_{OL} is an effective Hamiltonian able to induce a two phonon process. The term in brackets is of the same order of magnitude as a one ion relaxation rate W_{rel} between $|^1\text{G}_4(9)\rangle$ and $|^1\text{G}_4(8)\rangle$ which would create two phonons of a total energy of 265 cm^{-1} instead of 336 cm^{-1} for a real relaxation between these states. This rate is itself of the same order of magnitude of rates involving similar phonons which can be deduced from linewidth measurements [19]. Equation (2) can thus be written as :

$$W \sim \frac{|\langle I | H_c | i \rangle|^2}{(E_i - E_f)^2} W_{\text{rel}} \quad (3)$$

with

$$10^{-12}\text{ s}^{-1} < W_{\text{rel}} < 10^{-11}\text{ s}^{-1}. \quad (4)$$

The ion-ion interaction is estimated in the case where it is multipolar electric using the calculations of Kushida [20] and the wavefunctions of Weber [21]. For two ions at $5\text{ \AA}$ one from another, the results are :

$$\begin{array}{ll} \text{dipole-dipole} & |\langle i | H_c | I \rangle| \sim 5 \times 10^{-4}\text{ cm}^{-1} \\ \text{dipole-quadrupole} & |\langle i | H_c | I \rangle| \sim 1.5 \times 10^{-3}\text{ cm}^{-1} \\ \text{quadrupole-quadrupole} & \sim 0. \end{array} \quad (5)$$

These weak values result from the spin-forbidden matrix elements between $^3\text{P}_0$ and $^1\text{G}_4$ and between $^3\text{H}_4$ and $^1\text{G}_4$; the zero value for quadrupole-quadrupole interaction results from J selection rule between $^3\text{P}_0$ and $^1\text{G}_4$. Using (4) and (5), the transition probability (2) is estimated

to be :

$$\begin{aligned} \text{dipole-dipole} & \quad 5 \text{ s}^{-1} < W < 50 \text{ s}^{-1} \\ \text{dipole-quadrupole} & \quad 50 \text{ s}^{-1} < W < 500 \text{ s}^{-1} . \end{aligned}$$

These rates are very small compared to the measured $97\,000 \text{ s}^{-1}$ and $25\,000 \text{ s}^{-1}$ values for lines f and a. The upper limit for dipole-quadrupole interaction becomes however comparable with the rates observed for the lines b and e. Thus, a short range interaction has to be considered in order to explain the experimental measurements of the cross relaxation transfer rates.

1.3 INTERPRETATION OF FLUORESCENCE DECAY IN HEAVILY DOPED CRYSTALS. — Recently, Hegarty *et al.* [8] have studied the quenching of the $^3\text{P}_0$ fluorescence in heavily doped samples.

For a 20 % sample, they explain the observed $^3\text{P}_0$ fluorescence decay by any of the usual mechanisms. They note however the existence of an exponential tail at long times and they attribute it to special ions occupying « non quenching » sites. Subtracting this tail from the total signal, they obtain the decay of the « normal » ions which is in agreement with a dipole-dipole interaction.

It is shown here, that the observed signal can be interpreted by taking into account only transfer between the two ions of the pairs associated with satellites f and a. For that, it is necessary to recall some results on transfer in diluted systems. In a crystal doped with a concentration x , the fluorescence decay of the donor ions, in absence of back transfer, can be written as :

$$\phi(t) = e^{-W_r t} \prod_{\alpha} (x e^{-W_{\alpha} t} + 1 - x)^{N_{\alpha}} \quad (6)$$

where W_r is the radiative rate, W_{α} the non radiative cross relaxation rate induced by one of the N_{α} equivalent ions which make the class α of pairs with the central ion. The contribution to $\phi(t)$ of the class α is $(1 - x)^{N_{\alpha}}$ for $t \gg 1/W_{\alpha}$ and $(1)^{N_{\alpha}}$ for $t \ll 1/W_{\alpha}$. Since table I gives the values of the W_{α} for the various classes of pairs, it can be seen that in the time interval 100-200 μs , pairs associated with satellites f and a contribute to $\phi(t)$ by $(1 - x)^{N_f + N_a}$ while pairs associated with satellites b, e, c, d do not contribute significantly.

Thus, in this time interval :

$$\phi(t) \cong (1 - x)^{N_f + N_a} e^{-W_r t} . \quad (7)$$

This behaviour predicted from the results of table I is in qualitative agreement with the experimental $\phi(t)$ reported by Hegarty *et al.* [8] for $x = 0.20$ as shown in figure 3, since the exponential variation at long time with a rate W_r is indeed observed. The comparison between this decay and equation (7) gives the value of $(1 - x)^{N_f + N_a}$ from which one deduces $(N_f + N_a) \sim 9$. Thus, only cross relaxation between one ion and its possible 9 first neighbours has to be considered. However, by looking at the list of the pairs given by equation (1), one can hardly find what are the pairs associated with lines f and a. In the following, we suppose that the 6 classes of pairs of the first bracket are associated with satellite f ($N_f = 6$) and that the 4 classes of pairs of the second group in the second bracket are associated with satellite a. This choice is the weakness of our interpretation because it appears as an *ad hoc* choice. Indeed, if $N_f = 6$ can be justified by the near equivalence of the pairs of the first bracket, the single peculiarity which can be given to justify $N_a = 4$ is that the other 2 classes of pairs of the second bracket are pairs with an inversion centre. It must be recalled that peculiar and unexplained properties have already been reported for some Pr^{3+} pairs [20].

The decay given by equation (6) can then be calculated with only the two classes of pairs f and a, using $N_f = 6$, $N_a = 4$ and the values W_f and W_a of table I. The comparison with the experimental decay reported by Hegarty *et al.* [8] for a 20 % doped sample is shown in figure 3.

Fig. 3. — 3P_0 fluorescence decay of a $\text{LaF}_3 : 20\% \text{Pr}^{3+}$ sample. Points are experimental points as reported in reference [8]. The curve is $\phi(t)$ of equation (6) with $\alpha = f, a$, with W_f and W_a as given in table I and with $N_f = 6$, $N_a = 4$ as explained in the text.

The agreement is very good for the whole time domain studied. Thus, our description gives an alternative interpretation of the Hegarty *et al.* results which does not need to suppose the existence of special ions. Our description can also be used to predict the slopes s at $t = 0$ of a semi-log plot of $\phi(t)$. From equation (6) :

$$s = - \left[\frac{d}{dt} \ln \phi(t) \right]_{t=t_0} = W_r + x \sum_{\alpha} N_{\alpha} W_{\alpha} \quad (8)$$

s can be calculated with $W_r = 0.021 \mu\text{s}^{-1}$ and the values of W_f and W_a of table I and compared with experiment. Table II gives the results of this calculation and the experimental values for various concentrations. The experimental value for $x = 0.05$ is taken from a result observed at $T = 40 \text{ K}$ when the decay is exponential due to the diffusion among the Pr^{3+} ions [13]; as shown by Huber [22] the slope is also given by (8) in that case.

Table II shows that the agreement is very good for moderate concentrations and gives the proof that cross relaxation with the 10 near neighbours (at a distance of less than $4.42 \text{ \AA}$) dominates the quenching of the fluorescence. It is thought that the disagreement for higher concentrations results from the fact that the essential hypothesis made to establish equation (6), namely that all transfers occur between *two ions*, is no longer valid and that three (or more) ion quenching processes have then to be considered.

We conclude, from these three arguments, that indeed a short range interaction dominates multipolar interaction between Pr^{3+} ion. Representative values of this interaction can be deduced

from the experimental rates using equation (3) and the estimation (4) :

$$2 \times 10^{-2} < |\langle i | H_c | I \rangle| < 7 \times 10^{-2} \text{ cm}^{-1} \quad \text{for line f}$$

$$10^{-2} < |\langle i | H_c | I \rangle| < 3.5 \times 10^{-2} \text{ cm}^{-1} \quad \text{for line a.}$$

Table II. — *Calculated and observed values of the slope s (in μs^{-1}) at $t = 0$ of the $^3\text{P}_0$ fluorescence decay for various concentrations x of Pr^{3+} in LaF_3 (see Eq. (8)).*

x	Calculated	Experimental	Refs.
1	0.70	1.32	[12]
0.8	0.54	0.80	[10]
0.5	0.36	0.44	[12]
0.2	0.16	0.14	[8]
0.05	0.055	0.056	[13]

These values compare well with those obtained by a direct measurement using a two laser spectroscopy technique [23] which are of the order of 0.2 to 0.5 cm^{-1} . All these values are compatible with some estimations by Birgeneau [1] of the superexchange coupling. The structure of LaF_3 is also in favour of this coupling since for the first four classes of pairs of the list (1) (i.e. in the first two brackets, the two ions have in common respectively : 2, 1, 2, 1 F^- ions when considering a coordination polyhedron of 9 ligands (maximum La-F distance : 2.62 Å) and 3, 3, 2, 2 F^- ions when considering a coordination polyhedron of 11 ligands (maximum La-F distance 3.08 Å)).

The above values are also of the same order of magnitude as those deduced by Meltzer and Moos [24] from the lineshape and position of the magnon-exciton transitions in GdCl_3 and $\text{Gd}(\text{OH})_3$ and attributed to exchange interaction between Gd^{3+} ions. The more recent results of Cone and Meltzer on $\text{Tb}(\text{OH})_3$ [25] also indicate the predominance of exchange interaction for some exciton dispersion.

To summarize, the direct measurement of cross relaxation rates between ions associated in pairs has been used to show that the quenching of $^3\text{P}_0$ fluorescence results essentially from the interaction between one Pr^{3+} and its possible 10 Pr^{3+} nearest neighbours. This interaction is thus of short range and arguments are given to show that it is superexchange. Although the efficiency of this mechanism was already observed for GdCl_3 , $\text{Gd}(\text{OH})_3$, $\text{Tb}(\text{OH})_3$ from measured exciton dispersion [24, 25], a proof based on direct measurement of transfer rates has not yet been presented. The values of the cross relaxation rates measured on the well isolated pairs present in weakly doped crystals are also used to calculate the behaviour of heavily doped crystals, making thus the first connection between directly measured microscopic and macroscopic quantities. The comparison of this calculated behaviour with experiments is very good and indicates the probable efficiency of processes involving more than two ions when the concentration exceeds 50 %. It is hoped that the connection between microscopic properties and the collective behaviour in stoichiometric crystals will also be possible.

Acknowledgments. — It is a pleasure for the authors to thank F. Madéore for his technical assistance and R. Romestain for a critical reading of the manuscript. They also wish to thank W. M. Yen for sending his review paper and other papers prior to their publication.

References

- [1] BIRGENEAU, R. J., *Appl. Phys. Lett.* **13** (1968) 193.
 - [2] INOKUTI, M., HIRAYAMA, F., *J. Chem. Phys.* **43** (1965) 1978.
 - [3] DORNAUF, H., HEBER, J., *J. Lumin.* **22** (1980) 1.
 - [4] SIEBOLD, H., HEBER, J., *J. Lumin.* **22** (1981) 297.
 - [5] HEGARTY, J., HUBER, D. L., YEN, W. M., *Phys. Rev. B* **23** (1981) 6271.
 - [6] BUISSON, R., VIAL, J. C., *J. Physique-Lett.* **42** (1981) L-115.
 - [7] WATTS, R. K., in *Optical Properties of ions in solids*, edited by Di Bartolo, B. (Plenum, New York) 1975.
 - [8] HEGARTY, J., HUBER, D. L., YEN, W. M., to be published in *Phys. Rev. B*.
 - [9] CARNALL, W. T., FIELDS, P. R., SARUP, R., *J. Chem. Phys.* **51** (1969) 2587.
 - [10] YEN, W. M., in *Spectroscopy of 4f ions in crystals*, edited by MacFarlane, R.M. (North Holland) to be published.
 - [11] BROWN, M. R., WHITING, J. S. S., SHAND, W. A., *J. Chem. Phys.* **43** (1965) 1.
 - [12] LAI, S. T., SHIHUA HUANG, YEN, W. M., to be published in *Phys. Rev. B*.
 - [13] FLACH, R., HAMILTON, D. S., SELZER, P. M., YEN, W. M., *Phys. Rev. B* **15** (1977) 1248.
 - [14] VIAL, J. C., BUISSON, R., MADÉORE, F., POIRIER, M., *J. Physique* **40** (1979) 913.
 - [15] Values slightly different can be found in the literature. For this paper, the absolute value is unimportant and it is sufficient that τ and τ_0 have been measured in similar experimental conditions.
 - [16] KAPLAYANSKII, A. A., PRZHEVUSKII, A. K., *Sov. Phys. Solid State* **9** (1967) 190 and MOLLENAUER, L. F., SCHAWLOW, A. L., *Phys. Rev.* **168** (1968) 309.
 - [17] VON MANSMANN, M., *Z. Kristallogr.* **122** (1965) 375.
 - [18] HOLSTEIN, T., LYO, S. K., ORBACH, R., *Phys. Rev. B* **15** (1977) 4693.
 - [19] YEN, W. M., SCOTT, W. C., SCHAWLOW, A. L., *Phys. Rev.* **136** (1964) A 271.
 - [20] KUSHIDA, T., *J. Phys. Soc. Japan* **34** (1973) 1318.
 - [21] WEBER, M. J., *J. Chem. Phys.* **48** (1968) 4774.
 - [22] HUBER, D. L., *Phys. Rev. B* **20** (1979) 2307.
 - [23] VIAL, J. C., BUISSON, R., *J. Physique-Lett.* **43** (1982) L-339.
 - [24] MELTZER, R. S., MOOS, H. W., *Phys. Rev. B* **6** (1972) 264.
 - [25] CONE, R. L., MELTZER, R. S., *J. Chem. Phys.* **62** (1975) 3573.
-