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Multiphoton excitations in neodymium chlorides

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Several multiphoton absorptions have been observed in Nd^{3+}:$La_xCe_{1-x}Cl_3$ crystals. Preliminary results and an attempted interpretation are presented.

INTRODUCTION

The absorption and fluorescence spectra of the trivalent neodymium ion in crystals of anhydrous chloride diluted with $LaCl_3$ are very well known, and quantum-number assignments have been made for all observed energy levels of the $4f^3$ configuration.[1,2] The spectra of the neodymium ion in anhydrous chloride diluted with $CeCl_3$ crystals, isomorphous in structure to $LaCl_3$ crystals, have not been so extensively studied. However, it has been shown that there is virtually no shift of the electronic lines when the lanthanum ions are completely replaced by cerium ions.[3]

In the mixed Nd:$(La_xCe_{1-x})Cl_3$ crystals with $0 \leq x \leq 1$, we have detected several narrow excitations occurring in the transparent regions, and giving rise to a very intense fluorescence spectrum of the neodymium. Some experimental results are presented here, together with a tentative interpretation involving a multiphoton-absorption process.

EXPERIMENTAL RESULTS

The crystals used for this study contained 1% or 0.05% $NdCl_3$ in $LaCl_3$ and $CeCl_3$. The mixed crystals contained only traces of neodymium. The samples were cooled in a CF 204 Oxford Instruments continuous-flow cryostat which allows the temperature to be varied from 4 to 300 K.

Fluorescence spectra were produced by excitation with a tunable rhodamine 6*G* single-mode cw ring laser (Spectra Physics, model No. 380) and analyzed with a grating monochromator (Jobin Yvon model THR). An accurate measurement of the excitation wave numbers was obtained by use of a Lambdascope.[4]

The laser frequency was scanned between 17 000 and 17 200 cm^{-1}. In addition to the fluorescence produced by absorption of the laser energy corresponding to the well-known electronic allowed Nd transitions ${}^4I_{9/2}(\frac{5}{2}) \rightarrow {}^4G_{5/2}(\frac{1}{2},\frac{3}{2})$, a neodymium fluorescence occurs for some laser frequencies which do not correspond to absorption energies. All these "excitation lines," never reported before, produce the whole Nd$(La_xCe_{1-x})Cl_3$ fluorescence spectrum, which has been recorded here in the spectral range between near ultraviolet to near infrared.

TABLE I. Excitation lines in Nd^{3+}:$LaCl_3$ and possible ion pair absorption lines (the excited states of first and second ion are noted with their symbols and the sum σ of their respective wave numbers).

σ_{el} (cm^{-1})	Excited states of ion pair	$\sigma_1+\sigma_2$ (cm^{-1})
17 038	$X_5\,{}^4I_{13/2}(\frac{1}{2})+M_1\,{}^2L_{15/2}(\frac{3}{2})$	34 074.7
17 104.45	$S_5\,{}^2H_{9/2}(\frac{3}{2})+G_{14}\,{}^2K_{15/2}(\frac{1}{2})$	34 208.9
	$X_1\,{}^4I_{13/2}(\frac{1}{2})+{}^4D_{7/2}(\frac{3}{2})$	34 208.85
17 108.8	${}^2H_{9/2}(\frac{1}{2})+G_{12}\,{}^2K_{15/2}(\frac{1}{2})$	34 217.4

Some of the excitation lines (EL) are extremely intense, polarized and very narrow ($\sim$0.5 cm^{-1}). The wave numbers of the excitation lines in $LaCl_3$ are reported in Table I. From $LaCl_3$ to $CeCl_3$ the excitation lines exhibit a red shift whose magnitude is similar to the electronic line shift.

Curiously the existence of the excitation lines depend on both the neodymium and cerium concentrations simultaneously. For cerium concentrations as low as a few percent, the σ_{EL} radiation excites the fluorescence even when neodymium is present as traces only (10^{-3}–10^{-4} %). In $LaCl_3$ crystals, on the contrary, no fluorescence appears when the concentration in Nd ions is 5×10^{-2}%, but it is very intense when the concentration is 1%.

Another uncommon feature of the phenomenon is the time required for the process to stabilize (a few seconds, as can be seen in Fig. 1).

The fact that the excitation lines appear in completely transparent regions in the spectral range investigated has been verified by means of an absorption spectrum, eliminating the possibility of the presence of absorbing impurities. This implies that the fluorescence is not induced by a single-photon absorption and suggests that the ions are

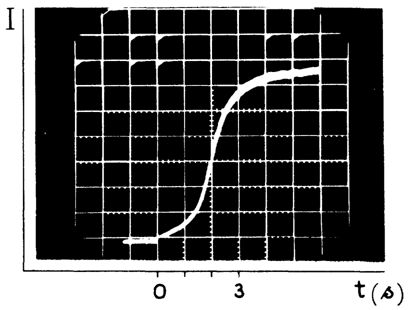

FIG. 1. Oscilloscope traces of the 17 104.45-Å excitation-induced fluorescence, obtained with a 1% Nd:$LaCl_3$ sample cooled at 4 K.

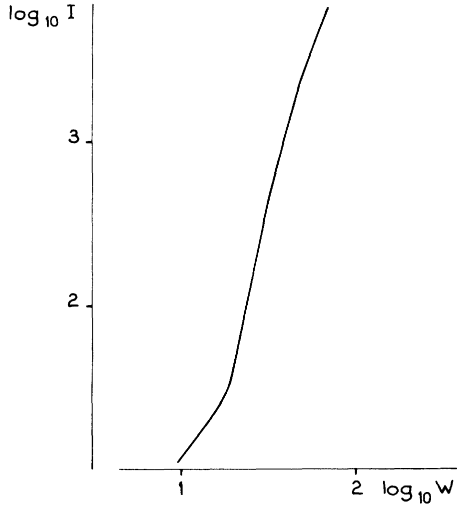

FIG. 2. Example of a fluorescence intensity dependence as a function of the laser power, obtained with a 1% Nd:LaCl$_3$ sample cooled at 4 K and a 17 104.45-Å excitation. (I and W are in arbitrary units.)

excited through a multiphoton process.

A typical feature of multiphoton processes is the power dependence of the transition probabilities, which in most cases reflects the number n of photons absorbed: The fluorescence intensity I is expected to vary as W^n, W being the laser power. In our experiments, the slopes of the curves I versus W in a log-log plot are actually larger than 1, which confirms our interpretation in terms of multiphoton process. However, the slopes obtained are drastically dependent on the experimental conditions. Moreover, they are not a constant when W is varied (Fig. 2) and can exhibit values up to 10.

Given the importance of the discrepancies, we have undertaken a systematic study of the possible sources of error: (1) the changes in the geometry of the incident beam occurring during the experiment; (2) the laser heating of the sample which deeply distorts the meaning of the $I=f(W)$ measurements since the intensity of the fluorescence induced by excitation of the EL lines is very sensitive to the temperature of the sample (Fig. 3).

Neither of these errors can really be overcome. For this reason, a valid estimation of the multiphoton cross sections cannot be reasonably made.

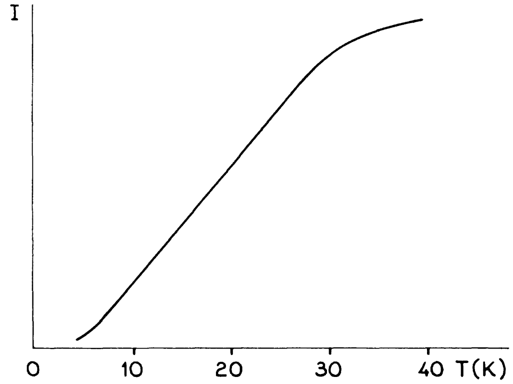

FIG. 3. Fluorescence intensity dependence as a function of the temperature obtained with a 17 104.45-Å excited 1% Nd:LaCl$_3$ sample.

DISCUSSION

Multiphoton processes are widely investigated in rare-earth compounds. Concerning the chlorides, as early as 20 years ago a visible fluorescence, produced by the 1.06-μm radiation of a Nd:YAG (yttrium aluminum garnet) laser, was observed in pure NdCl$_3$. It was attributed to a four-photon sequential process involving two double-photon transitions.[5]

The development of tunable lasers has led to more accurate experiments in diluted rare-earth lanthanum chlorides. The up-conversion phenomenon is a large subject of interest. It is now possible to attribute its origin either to a sequential absorption in one center or to a cooperative process.[6,7] The two-photon absorption technique (TPA) allows precise measurements of weak intraconfiguration transitions.[8]

These various processes cannot account for the observed phenomenon we present here.

It cannot be an up-conversion process whose characteristic is that the fluorescence exhibits a square-intensity power dependence when the observed emitting level has an energy higher than the excitation energy. On the contrary, the excitation lines we are dealing with exhibit an intensity power dependence absolutely independent of the emitting level, whatever its energy is, whether higher or lower than the excitation energy.

It cannot be a now-classical TPA. As a matter of fact, at frequencies twice the excitation line frequency a single ion cannot possibly absorb because there are no absorbing levels at these frequencies.[2]

Given the intensities of the lines, an excitation through a forbidden transition must be thrown away. Therefore it cannot be a three-photon absorption in the $4f^3$ configuration (besides the fact that no level of this configuration exists at frequencies three times the excitation-line frequencies) nor an absorption by a triad of Nd ions.

As stated before, experimental difficulties prevented us from establishing definitely the number of quanta involved in the process. Nevertheless, assuming that the high values of the slopes are a temperature effect, we present interpretations using both hypotheses of a two-photon and of a three-photon process. For each we take into consideration the fluorescence-intensity enhancement due to the presence of cerium.

Hypothesis of a two-photon excitation process

To satisfy this hypothesis, the existence of a cooperation of pairs of Nd ions is necessary.

The possibility of a weak absorption of one photon by two ions simultaneously was demonstrated on concentrated praseodymium chloride,[9,10] in agreement with nonlinear coupling between neighboring Pr^{3+} ions.

In the case of neodymium chloride, the energies of the "excitation lines" can be accounted for, within 1 cm^{-1}, by half the sum of two Nd absorption transitions from the ground state (Table I) and their intensities by the fact that the excitation is a two-photon one. For single ion levels and pairs of ion levels all belonging to the $4f^3$ configuration, the excitations correspond to parity-allowed transitions, the intermediate states being derived from parity mixing induced by odd terms in the crystal-field potential or by phonon assistance from odd-parity vibrational modes. The small energy mismatches between the photons and the electronic states explain the intensity and the resonant character of the lines.

To account for the enhancement of the fluorescence due to the presence of cerium in the host, it has to be assumed that Ce^{3+} ions, by one way or another, favor the probability of clustering of Nd^{3+} ions.

Hypothesis of a three-photon excitation process

A three-photon transition is parity allowed only if the Nd ions are excited in the $4f^25d$ configuration, which is possible as the lowest level is thought to be around 44 800 cm^{-1}.[2] But the 5*d* Stark levels are broad bands, and the configuration can be considered as a continuum. It is therefore impossible to make a correspondence between the recorded sharp lines and transitions to the $4f^25d$ levels.

To account for the observed spectrum, it has to be assumed that it represents the probability density of the three-photon transition. This density depends on the product of the overlaps of the electronic and vibronic wave functions of the states in the two intermediate regions. Therefore it has also to be assumed that the more or less intense discrete peaks in the spectrum result from constructive interferences in this product. A Nd^{3+} concentration minimum is required for a nonnegligible absorption in the $4f^25d$ bands to occur. This absorption exists for very low concentrations in Nd^{3+} ions provided that all or part of the La^{3+} ions are replaced by Ce^{3+} ions in the host. Under this condition it must be assumed that the three-photon transition is, via neodymium intermediate states, towards the 5*d* bands of cerium (from[11] the bottom of the configuration this is estimated to be around 38 000 cm^{-1}), and that the energy absorbed by the Ce^{3+} ions is used to populate excited states of neodymium by energy transfer.

CONCLUSION

New excitation lines, not mentioned until now to our knowledge, have been observed in the $Nd(La_xCe_{1-x})Cl_3$ system and are undoubtly related to a multiphoton process. The results presented here are only preliminary, but the phenomenon appears very interesting because of its unusual nature: the absorption is not resonant with any narrow electronic level of a neodymium ion, the process needs a few seconds to be established and is enhanced by the presence of cerium.

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[1] H. M. Crosswhite, H. Crosswhite, F. W. Kaseta, and R. Sarup, J. Chem. Phys. **64**, 1981 (1976).

[2] R. S. Rana, F. W. Kaseta, and R. H. Garvey, J. Chem. Phys. **77**, 4400 (1982).

[3] C. K. Asawa, Phys. Rev. **155**, 188 (1967).

[4] N. Pelletier-Allard and R. Pelletier, Rev. Sci. Instrum. **55**, 1442 (1984).

[5] S. Singh and J. E. Geusic, in *Optical Properties of Ions in Crystals*, edited by H. M. Grosswhite (Interscience, New York, 1967); Phys. Rev. Lett. **17**, 865 (1966).

[6] D. J. Zalucha, J. A. Sell, and F. K. Fong, J. Chem. Phys. **60**, 1660 (1974).

[7] N. Pelletier-Allard and R. Pelletier, J. Phys. (Paris) **43**, 403 (1982).

[8] R. S. Rana, C. D. Cordero-Montalvo, and N. Bloembergen, J. Chem. Phys. **81**, 2951 (1984).

[9] F. Varsanyi and G. H. Dieke, Phys. Rev. Lett. **7**, 442 (1961).

[10] G. H. Dieke and E. Dorman, Phys. Rev. Lett. **11**, 17 (1963).

[11] F. A. Kröger and J. Barker, Physica **8**, 628 (1941).