PHYSICAL REVIEW B VOLUME 46, NUMBER 10 1 SEPTEMBER 1992-II

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Photon-assisted off-resonance energy transfer between Cr^{3+} and Gd^{3+} in $GdAlO_3$

José L. Duarte* and Jarbas C. Castro

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560 São Carlos, São Paulo, Brazil

(Received 19 February 1992)

We report here a clear observation of photon-assisted off-resonance energy transfer. Our experiment was carried out in crystals of gadolinium aluminate ($GdAlO_3$) doped with chromium ions (Cr^{3+}). The observed phenomenon consists of the energy transfer from a Cr^{3+} ion, previously excited to the ^2E state (located at about 13.770 cm^{-1} above the ground state), to a neighbor Gd^{3+} ion (which has the first excited state located at about 31.840 cm^{-1}), with the simultaneous absorption of a photon that energy matches exactly the difference between the gadolinium excited-state energy and the energy supplied by the chromium ion.

I. INTRODUCTION

Interactions between ions in solids may initiate electronic transition processes such as cooperative absorption,[1] cooperative luminescence,[2] and nonradiative energy-transfer processes that cannot be explained by considering isolated ions.

Nonradiative energy-transfer processes have been the object of great interest recently,[3–6] making it possible to develop more efficient laser materials,[7] to increase the sensitivity of infrared quantum counters,[8] and to construct tunable light-emitting diodes in the visible region.[9] The application of these processes in the development of more efficient solar cells has also been investigated.[10]

The systems that have often been used in research in this area are crystals (or glasses) doped with either rare-earth ions or rare-earth ions and other ions.

Among the nonradiative energy-transfer processes, one of particular interest, studied here, is photon-assisted off-resonance energy transfer (PAORET). The PAORET process between two ions in solids was theoretically predicted in 1970 by Altarelli and Dexter[11] and more recently treated by other authors.[12]

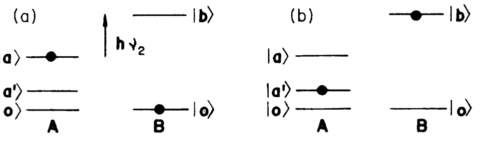

FIG. 1. Scheme of the photon-assisted off-resonance energy-transfer (PAORET) process from an ion A to an ion B. (a) The system is prepared with ion A previously excited, and a second photon of frequency ν_2 interacts with both ions; (b) energetic status of the ions A and B after simultaneous energy transfer and absorption of a photon with energy $h\nu_2 = E_b - (E_a - E_{a'})$.

In the PAORET process an excited donor ion can transfer its energy to an acceptor ion with the simultaneous absorption of a laser photon, resulting in an excited acceptor ion with energy equal to the sum of the energy supplied by the donor and the absorbed photon energy. The electronic energy status of the system, before and after the occurrence of the PAORET process, are schematically shown in Fig. 1. This process is the inverse of experimentally observed Raman luminescence.[13] In atomic physics a process similar to PAORET, referred as a "laser-induced inelastic collision," was theoretically proposed[14] and experimentally observed.[15]

We present here a clear observation of the PAORET process in solid-state physics, although some early experimental results have indicated its occurrence.[16]

Our experiment was carried out in crystals of gadolinium aluminate ($GdAlO_3$) doped with chromium, where

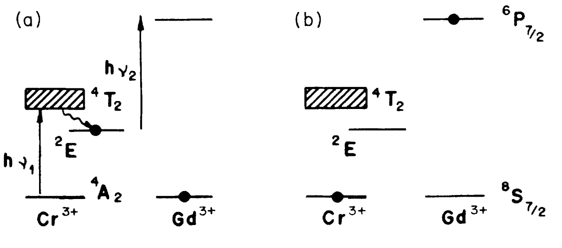

FIG. 2. Energy levels of interest and photon involved in the experiment. (a) Status of the system after excitation of the metastable ^2E level of Cr^{+3} through a $^4T_2$ broad absorption band of it. The energy of the ^2E state of Cr^{3+} is ~ 13.700 cm^{-1}, and the first $^6P_{7/2}$ substate of Gd^{3+} is 31.837 cm^{-1} above the ground state. ν_1 is the argon-laser photon, and ν_2 is the tunable dye-laser photon. (b) System after occurrence of PAORET.

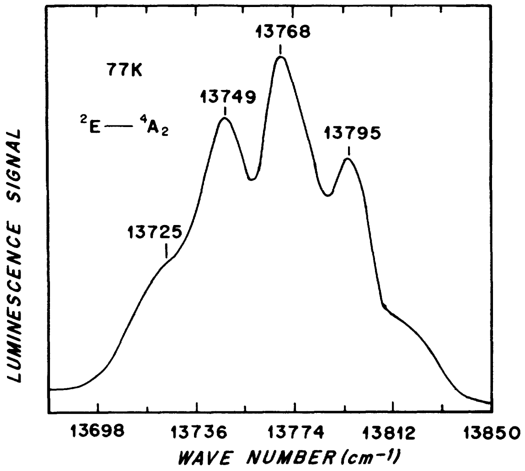

FIG. 3. Luminescence spectrum of the Cr^{3+} metastable state (^2E) in $GdAlO_3$ at liquid-nitrogen temperature (see Ref. 17).

the triply ionized chromium replaces the also triply ionized aluminum of the lattice. The energy transfer happens from the Cr^{3+} ion to the Gd^{3+}-lattice ion. The fact that the Gd^{3+} ions belong to the crystal lattice assures that all the Cr^{3+} ions are interacting with them, even at low Cr^{3+} concentration in the crystal, and then all of the Cr^{3+} ions are able to contribute to the PAORET process. In Fig. 2 we present a simplified scheme of the process, where the energy levels that are of interest for the present experiment are shown. The Cr^{3+}-ion metastable state (^2E), which has a long lifetime[17] (approximately 11 ms), is excited by the green line (514 nm) of a cw argon-ion laser through the intermediate state $^4T_2$. The PAORET phenomenon takes place in this system when the photons of a second laser reach an energy ($h\nu_2$) equal to the difference between the Gd^{3+} $^6P_{7/2}$ excited-state energy and the energy supplied by the Cr^{3+} metastable state through nonradiative energy transfer ($^2E \Longrightarrow {}^4A_2$ transition).

Although the simplified energy-level scheme presented in Fig. 2 does not show this feature, the luminescence spectrum of the Cr^{3+} metastable state ($^2E \Longrightarrow {}^4A_2$ transition) presents a fine structure,[17] shown in Fig. 3, ascribed to the magnetic Franck-Condon effect.[18]

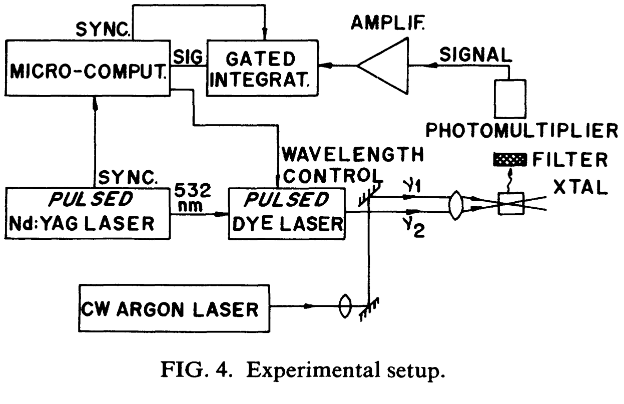

FIG. 4. Experimental setup.

II. EXPERIMENTAL DETAILS

We used in this experiment $GdAlO_3$ crystals containing approximately 0.1 at. % chromium. The samples were grown by a high-temperature solution technique.[19] In the growing process color centers may be formed.[20] The presence of these centers in the samples used was easily detected by luminescence.[21,22]

The space group of $GdAlO_3$ is D_{2h}^{16} (P_bnm).[23] The Gd^{3+} ion has Cs-site symmetry and Cr^{3+} substitutes Al^{3+}, which has Ci site symmetry.

The experimental setup employed in this work is shown in Fig. 4. A commercial cw argon-ion laser and a homemade pulsed 5-ns dye laser pumped by the second harmonic of a commercial Nd:YAG laser are simultaneously focused and superposed in the same spot by a single lens in the $GdAlO_3$:Cr^{3+} sample.

The sample is kept at liquid-nitrogen temperature in a simple cryostat. The detection of the excitation of the Gd^{3+} ion by the PAORET process is done by monitoring the blue luminescence due to the decay of the lowest excited state ($^6P_{7/2}$) of the Gd^{3+} ion as explained in the next paragraph. The luminescence is detected by a photomultiplier, through a set of filters, as a function of the dye-laser frequency. The pulsed luminescence signal is amplified, integrated by a gate integrator, and fed in a PC-XT data-acquisition system, which also controls the dye-laser frequency.

The strong interaction and proximity of the Gd^{3+} ions between themselves favor the energy migration of the Gd^{3+} excitation through the gadolinium sublattice, and its decay occurs through chromium impurities or color centers unintentionally formed during the $GdAlO_3$ growth process, as the luminescence spectrum shows.[21,22] The Gd^{3+} excitation decay through the color center happens at a broadband (approximately from 14.000 to 28.000 cm^{-1}). The temporal evolution of this decay was previously measured[21] by exciting the $^6P_{7/2}$ Gd^{3+} lines with the second harmonic of a pulsed dye laser and showed an exponential decay time of 1 μs after laser excitation of Gd^{3+}.

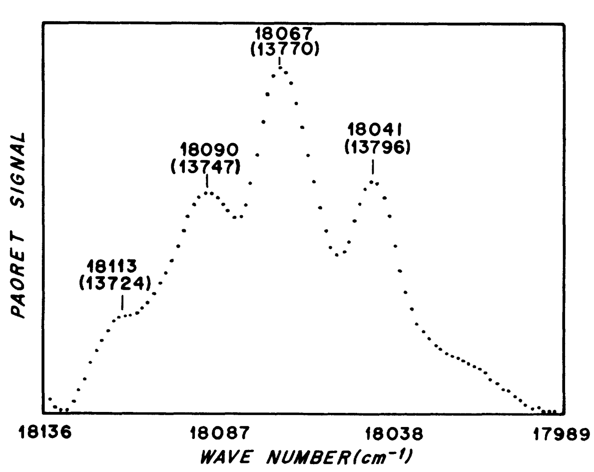

FIG. 5. PAORET signal as function of the dye-laser frequency. The upper numbers and numbers within brackets are explained in the text.

Because of the fact that the emission after Gd^{3+} excitation happens at a broadband and is much faster (1 μs) than the Cr^{3+} decay time (11 ms), we performed, in detecting the PAORET process, a double-filtering of the luminescence signal: a spectral filtering by detecting the luminescence through an optical filter that transmits light only at frequencies above all the ones of the lasers employed in the experiment and a temporal filtering by doing a gate integration of the signal with a 2-μs gate synchronized to the laser pulse.

III. RESULTS

In Fig. 5 we show the PAORET signal as function of the dye-laser frequency. The dye-laser frequency scans the region around the difference between the energy of the ^2E Cr^{3+} state and the first of the $^6P_{7/2}$ substates of the Gd^{3+} ion. The upper numbers in Fig. 5 indicate the frequencies of the dye laser corresponding to the peaks of the PAORET signal and the numbers within brackets correspond to the energy difference between the energy of the first of the $^6P_{7/2}$ substates of Gd^{3+} (31 837 cm^{-1}) and that of the corresponding peak. This spectrum was achieved only with the argon laser on and with its beam well superimposed to the dye-laser beam.

IV. DISCUSSION

Comparing the PAORET spectrum of Fig. 5 to the Cr^{3+} luminescence spectrum of Fig. 3, we verify their great similarity in shape, although in a completely different spectral range. In fact, the energy registered in the spectrum of Fig. 5 is, within the experimental error, the difference between the energy of the first $^6P_{7/2}$ sublevel of the Gd^{3+} ion (31.837 cm^{-1}) and the energy of emission in the Cr^{3+} luminescence spectrum shown in Fig. 3. We can therefore conclude that the dye-laser photons are absorbed when the energy of each one is equal to the difference between the energy of the $^6P_{7/2}$ level of the Gd^{3+} spectrum and the energy granted by the Cr^{3+} ion in the nonradiative transition $^2E \Longrightarrow {}^4A_2$. This interpretation of the phenomenon is schematically shown in Fig. 6, where the straight arrows stand for energy transfer and the undulated ones for its absorption.

The shape of the PAORET spectrum agrees with the theoretical prediction[11] which forsees a spectral line shape $S(E_2)$ equal to the integral convolution:

$$S(E_2)=\int S^{\rm em}_{a\to a'}(E)S^{\rm abs}_{0\to b}(E_2+E)dE\ , \tag{1}$$

where $S^{\rm em}_{a\to a'}(E)$ is the emission line shape of the ion A (Cr^{3+} in our case) and $S^{\rm abs}_{0\to b}$ is the absorption line shape of the ion B (Gd^{3+} in our case), with all line shapes normalized. In fact, Eq. (1) expresses energy conservation in the PAORET process. Because of the fact that $^6P_{7/2}$ sublevels of Gd^{3+} are very narrow[21,22] compared with the Cr^{3+} energy levels involved in the experiment, we can consider them as a δ function, $\delta(E-E_f)$, where E_f, in this case, is the energy of the lowest sublevel of the $^6P_{7/2}$ multiplet of Gd^{3+}. Therefore, Eq. (1) is simplified to

$$S(E_2)=S^{\rm em}_{a\to a'}(E_f-E_2)\ , \tag{2}$$

which represents very well the spectrum of Fig. 5, as compared with Fig. 3, taking into account the energy levels and laser frequencies involved in the experiment.

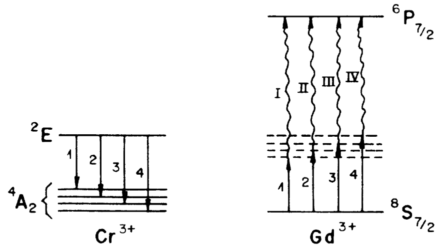

FIG. 6. Schematic representation of the PAORET phenomenon in the system $GdAlO_3$:Cr^{3+}, where the magnetic Franck-Condon fine structure in the ground state $^4A_2$ of Cr^{3+} is shown. The transitions 1, 2, 3, and 4 (represented by the straight arrows) of the level ^2E of Cr^{3+} to the sublevels of the ground state $^4A_2$ are nonradiative. It occurs simultaneously with the absorptions of, respectively, I, II, III, and IV (represented by the undulated arrows) photons. Dashed lines are virtual states, not levels of Gd^{3+}.

V. CONCLUSIONS

We have observed the photon-assisted off-resonance energy-transfer process between Cr^{3+} and Gd^{3+} in $GdAlO_3$. The spectrum obtained by detecting the emission due to the Gd^{3+} excitation shows in detail the structure of the Cr^{3+} $^4A_2$ ground state when the laser that induces the process scans the spectral region around the energy difference between the energy of the $^2E\rightarrow{}^4A_2$ transition of Cr^{3+} and the energy of the first $^6P_{7/2}$ sublevel. This is an unambiguous characterization of the occurrence of the PAORET process in $GdAlO_3$:Cr^{3+}.

ACKNOWLEDGMENTS

We would like to thank Professor José Pedro Andreeta for kindly supplying us with the crystals employed in this experiment and Professor Luiz Antonio de Oliveira Nunes, Professor Michel André Aegerter, and Professor Maria Cristina Terrile for helpful discussions. One of us (J.L.D.) thanks Coordenacão de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), from Brazil, for partial support.

---

*Permanent address: Departamento de Física, Universidade Estadual de Londrina, Caixa Postal 6001, Lodrina, PR, 86051, Brazil.

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

[2] E. Nakazawa and S. Shionoya, Phys. Rev. Lett. **25**, 1710 (1970).

[3] R. L. Cone and R. S. Meltzer, in *Spectroscopy of Solids Containing Rare Earth Ions,* edited by V. M. Agranovitch and A. A. Maradudin (North-Holland, Amsterdam, 1987), p. 544.

[4] J. C. Wright, in *Radiationless Processes in Molecules and Condensed Phases,* edited by F. K. Fong (Springer, New York, 1976), p. 239.

[5] *Laser Spectroscopy of Solids,* edited by W. M. Yen and P. M. Seltzer (Springer, New York, 1981).

[6] L. A. Riseberg and M. J. Weber, in *Progress in Optics,* edited by E. Wolf (North-Holland, New York, 1976), Vol. 14, p. 91.

[7] A. M. Prokhorov, Usp. Fiz. Nauk **148**, 7 (1986) [Sov. Phys. Usp. **29**, 3 (1986)].

[8] F. E. Auzel, P. A. Santa Cruz, and G. F. de Sá, Rev. Phys. Appl. **20**, 273 (1986).

[9] G. F. de Sá, P. A. Santa Cruz, and F. E. Auzel, J. Lumin. **31/32**, 693 (1984).

[10] C. Parent, C. Lurin, G. Le Flem, and P. Hangenmuller, J. Lumin. **36**, 49 (1986).

[11] M. Altarelli and D. L. Dexter, Phys. Rev. B **7**, 5335 (1973); Opt. Commun. **2**, 36 (1970).

[12] J. F. Lam and S. C. Rand, Phys. Rev. A **35**, 2164 (1987); J. Jortner and A. Ben-Reuven, Chem. Phys. Lett. **41**, 401 (1976); I. Kaplan and J. Jortner, *ibid.* **51**, 1 (1977).

[13] J. P. van der Ziel and L. G. Van Uitert, Phys. Rev. Lett. **21**, 1334 (1968); P. P. Feofilov and A. K. Trofimov, Opt. Spektrosk. **27**, 538 (1969) [Opt. Spectros. (USSR) **27**, 291 (1969)]; J. P. van der Ziel and L. G. Van Uitert, Phys. Rev. **186**, 332 (1969); Phys. Rev. **180**, 343 (1969); E. Nakazawa, J. Lumin. **12/13**, 675 (1973).

[14] L. I. Gudzenko and S. I. Yakovenklo, Zh. Eksp. Teor. Fiz. **62**, 1686 (1972) [Sov. Phys. JETP **35**, 877 (19782)]; S. E. Harris and D. B. Lidow, Phys. Rev. Lett. **33**, 674 (1974).

[15] R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A **15**, 1333 (1977).

[16] J. B. W. Morsink, J. A. C. Rullman, and D. A. Wiersma, J. Lumin. **24/25**, 767 (1981); S. Speiser, Appl. Phys. B **49**, 109 (1989); J. P. van der Ziel and L. G. van Uitert, Phys. Rev. B **8**, 1889 (1973); V. I. Bilac, G. M. Zverev, G. O. Karapetyan, and A. M. Onishchenko, Pis'ma Zh. Eksp. Teor. Fiz. **14**, 301 (1971) [JETP Lett. **14**, 199 (1971)].

[17] J. Murphy and R. C. Ohlman, in *Optical Properties of Ions in Crystals,* edited by H. J. Crosswhite and H. W. Moos (Interscience, New York, 1969).

[18] M. Matsuoka, M. A. Aegerter, H. Panepucci, M. C. Terrile, J. S. Helman, and H. J. Scheel, Phys. Rev. Lett. **50**, 204 (1983).

[19] H. J. Scheel, J. Cryst. Growth **13/14**, 560 (1972).

[20] V. A. Antonov, P. A. Arsenev, I. G. Linda, and V. L. Farshtendiker, Phys. Status Solidi A **15**, K63 (1973).

[21] J. L. Duarte, Ph.D. thesis, IFQSC-USP, São Carlos, SP, Brazil, 1990.

[22] L. A. O. Nunes, S. J. N. Pádua, and J. C. Castro, Phys. Rev. B **41**, 4736 (1990).

[23] S. Geller and V. B. Bala, Acta Crystallogr. **9**, 1019 (1956).