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INFRARED-OPTICAL DOUBLE RESONANCE IN RARE-EARTH CRYSTALS

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We have observed, at liquid-helium and liquid-hydrogen temperatures, strong well-polarized absorption lines originating from an optically populated level 2000 cm^{-1} above the ground state in Nd^{3+}(PrCl$_3$) crystals. The first stage of this double resonance process corresponds to infrared photons of about 5 μ. The second stage, marked "monitor" on Fig. 1, is a sensitive indicator of the population in the metastable infrared level which makes possible detailed relaxation measurements. It should be possible to extend these experiments further into the infrared and submillimeter region where they should provide a direct method for the study of relaxation processes in that unexplored region. Infrared quantum counter[1] action at 5 μ was also observed in this crystal. Considered as a scheme to detect infrared radiation, double resonance seems to compare favorably with existing far-infrared detectors.

In the experiments to be described here, the crystal, placed in the entrance focal point of a high-resolution spectrometer, was illuminated simultaneously with an infrared source which populated the $^4I_{11/2}$ level and a monochromatic beam which served as the monitor. In the present system, the metastable level can be populated either by direct absorption into sharp Nd^{3+} levels or into relatively broad bands of the PrCl$_3$ host (Fig. 1). Radiation absorbed in the praseodymium bands is efficiently transferred[2] to Nd^{3+} levels, and particularly to the Y_1 level. A globar or a 6-W tungsten lamp was used here as the infrared source. The strongest double-resonance signals observed were from the $^4I_{11/2}$ ($\mu \pm \frac{3}{2}$) neodymium level at 1975.84 cm^{-1} in PrCl$_3$ (called Y_1) to the two components

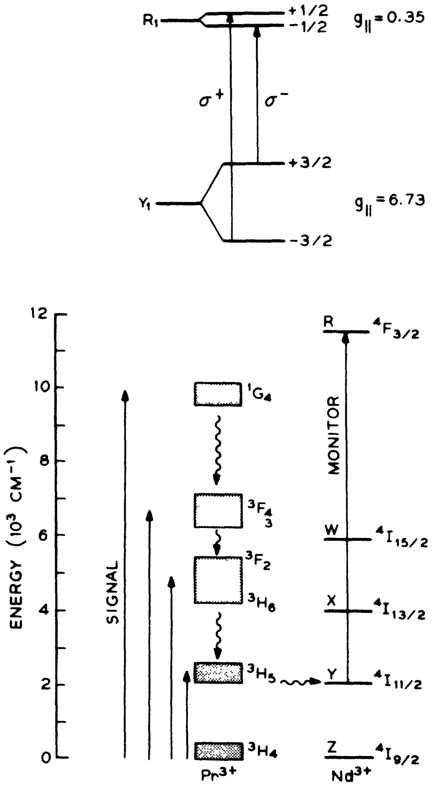

FIG. 1. The energy levels involved in the infrared double resonance. Absorption at the monitor wavelength of 1.06 μ is observed only when the infrared signal is received. Favorable wavelength regions where an incoming signal will populate the Y_1 level include the broad PrCl$_3$ bands and the sharp Nd^{3+} lines of the $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ levels. Energy absorbed in the PrCl$_3$ bands is transferred to the X_1 level as well, then part of it is transferred to Y levels by direct infrared fluorescence (see reference 2). This path is not indicated on the figure for clarity. The upper part indicates the Zeeman splitting and selection rules, for magnetic field parallel to crystal axis and electric dipole transitions.

of the $^4F_{3/2}$ level at 11 416.43 cm^{-1} ($\mu \pm \frac{1}{2}$) (called R_1) and 11 448.33 cm^{-1} ($\mu \pm \frac{3}{2}$) (called R_2). To observe these, the monitor source monochromator was set at 1.06 μ, and this beam entered the high-resolution spectrometer after passing through the crystal. Typical scans of the spectrometer are shown in Fig. 2. With the infrared source off, no absorption line is observed as shown on the uppermost trace, as neither Nd^{3+} nor the PrCl$_3$ host has energy levels in the corresponding 9400-cm^{-1} region. With the infrared source turned on, second trace, the strong $Y_1 \rightarrow R_1$ resonance signal was observed. The polarized Zeeman pattern of the $Y_1 \rightarrow R_1$ line is displayed on the third and fourth traces. The thorough polarization of the lines is remarkable. The pattern is exactly what is expected for pure electric dipole transitions. The corresponding Zeeman levels and g factors are shown on the upper part of Fig. 1. Also noteworthy is the high degree of spectral resolution demonstrated by the Zeeman pattern. This could not be obtained by direct infrared measurements with presently available instruments.[3]

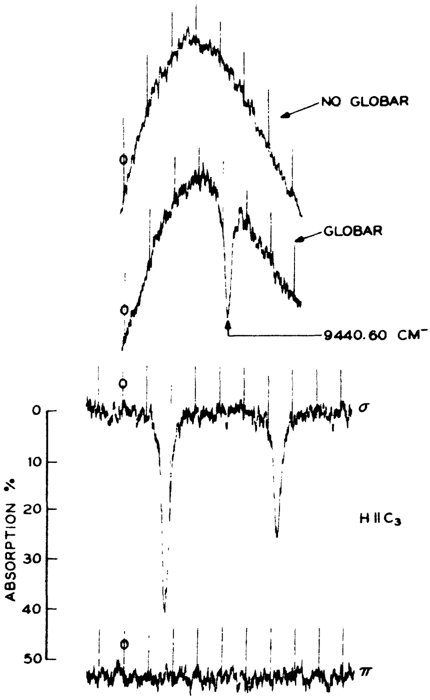

FIG. 2. Infrared double-resonance signal around 1.06 μ in Nd^{3+}(PrCl$_3$) single crystal at 20.4°K. Transition between $^4I_{11/2}(\mu\pm\frac{3}{2})$, 1975.84-cm^{-1} and $^4F_{3/2}(\mu\pm\frac{1}{2})$, 11 416.43-cm^{-1} levels. In the upper trace, no infrared pump is populating the 1976 level, so no resonance signal is observed. The middle trace was taken with a globar also focused on the crystal with an f:8 mirror. The curved background is indicative of the monitor beam monochromator output. On the lower traces, the crystal was subjected to a magnetic field while illuminated by a tungsten lamp which served both as signal and as monitor. The pattern unambiguously identifies the Y_1 and R_1 levels as initial and final states of the transition. The wavelength markers are 2.5 Å apart.

Double-resonance signals terminating on several other Nd^{3+} levels were also observed.[4] These are generally weaker than the $Y \rightarrow R$ lines where an unusually high transition probability connects the states. (All neodymium lasers operate between these two levels partly for the same reason.)

The population buildup and decay in the Y_1 level was studied by recording the intensity changes in the monitor beam while the infrared signal source was turned on and off with a fast shutter (10^{-3} sec). The monitor wavelength was in the photomultiplier region with correspondingly fast time response. We have measured the lifetime of the Y_1 level both by direct observation of the 5μ fluorescence and by double resonance, and found it to be about 85 msec at liquid-helium temperature.

We have also observed infrared quantum counter[1] action at 5 μ in the PrCl$_3$(Nd^{3+}) system at liquid-helium temperatures. Here the crystal, mounted in helium exchange gas at the cone-terminated end of a brass light-pipe, was illuminated with a globar source through the light-pipe and an InAs semiconductor filter. Only radiation with wavelengths longer than 3.6 μ could reach the crystal this way. Energy absorbed in the broad $^3H_5$ Pr^{3+} band and the sharp $^4I_{11/2}$ neodymium components populated the Y_1 level, then with a second absorption the X_1 neodymium level at 3931.96 cm^{-1} was reached and 2.54μ fluorescence detected with a spectrometer.[5] The excitation was chopped at 3 cps, and lock-in detection sensitive only to this frequency was used to observe the 2.54μ fluorescence. As a further check, Pyrex microscope slides were also interposed between globar and crystal in addition to InAs, and this completely stopped the fluorescence, indicating that it was not excited by spurious radiation with wavelengths shorter than 3.6 μ. The fluorescence was so intense that detailed time-behavior studies presented no difficulties.

Double-resonance experiments involving levels further out in the infrared and millimeter region seem very attractive. The feasibility will, of course, depend on the details of the relaxation processes which tend to prevent sufficient population buildup in levels too close to the ground state. But one should note that the requirements here are far less demanding than those to observe either spontaneous or stimulated emission of the corresponding far-infrared photons. The intensity of fluorescence rapidly diminishes because of the ν^3 dependence, and stimulated emission requires actual population inversion. Double resonance, on the other hand, requires only a relatively small population in the metastable level. Moreover, the detection is in the photomultiplier region, doing away with all difficulties connected with far-infrared detectors, optical window materials, etc. Since the metastable level can, in most cases, be populated by some indirect method, the study of a level corresponding to, for example, submillimeter wavelengths does not require either the generation or the detection of photons in this difficult region. The most attractive methods to populate these levels seem to be (a) fluorescence or laser transitions terminating here; (b) some use of rare-earth–rare-earth energy transfer as in the presently described system; (c) energy delivered to the fundamental lattice absorption and transferred to the active ion.

It is of some interest to evaluate the infrared optical double-resonance process as an infrared detection scheme, and also to compare it to the infrared quantum counter. The present $PrCl_3(Nd^{3+})$ system can be considered a broad-band infrared detector with sensitive regions wherever the crystal absorbs above the Y_1 level. As seen in Fig. 1, the Pr^{3+} bands cover infrared regions around 9900-9400 cm^{-1} ($^1G_4$), 7100-5920 cm^{-1} ($^3F_4$ and $^3F_3$), 5250-4080 cm^{-1} ($^3F_2$ and $^3H_6$), and 2700-2150 cm^{-1} ($^3H_5$), in addition to the Nd^{3+} levels. Projecting a similar scheme into the far-infrared region, the broad band could be the fundamental lattice absorption of the host, the metastable level some appropriate Stark component of the active ion ground state. In many cases[6] the higher ground-state Stark components extend up into the lattice vibration region, and these components as observed in fluorescence are broad, which for the present purposes can be considered as a guaranteed energy transfer mechanism from lattice vibrations to active ion.

Comparing now the two schemes, one can note that an infrared quantum counter requires two metastable levels,[7] one to be reached by the signal and the other with the pump, while the double-resonance process needs only one stable level[8] and the monitor wavelength can be chosen for best transition probability and photomultiplier sensitivity.[9] The response time will also be governed by two and one metastable states, respectively, in the two schemes. On the other hand, the detection of fluorescence is inherently easier than that of absorption because of the different frequency dependence. This is somewhat counterbalanced by the fact that the fluorescence is radiated into 4π solid angle, and in most cases transitions to other states than the ones detected as well as radiationless processes all compete with the detection. Nonetheless, in principle, the quantum counter can detect single incoming infrared photons and is noiseless,[10] while the double-resonance scheme has an inherent $\sqrt{n}$ noise due to the statistical fluctuation of the monitor beam intensity (n denotes the number of monitor photons per second). While compared to a truly noiseless system the $\sqrt{n}$ is very unfavorable, it is still a remarkable value,[11] being slightly better than the noise figure of masers. Extension into the far-infrared or millimeter regions meets with increasing filter difficulties with the quantum counter, as direct excitation from the ground state has to be prevented. This question does not arise with the double resonance where the presence of a direct ground-state absorption line in the monitor beam is immaterial as long as the lines are resolved beyond their width. In this respect, experiments[12] where changes in optical absorption are detected when ground-state Zeeman sublevels are saturated by microwave or radio-frequency radiation can be considered the limiting case of the double-resonance process discussed here. It is interesting to note that the other limiting case, on the high-frequency side, is the usually unwanted reabsorption[13] from the initial state of solid-state optical masers under high pumping intensities.

Finally, it is worth noting that the high spectral resolving power and fast detector response make infrared double resonance a promising tool for detecting microwave resonance in excited states[14] and thus studying spin-lattice relaxation processes.

Discussions with G. K. Wertheim, J. P. Gordon, and C. G. B. Garrett are greatly appreciated. The experimental assistance of B. Toth

was most valuable.

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[1] N. Bloembergen, Phys. Rev. Letters 2, 84 (1959).

[2] F. Varsanyi, Phys. Rev. Letters 11, 314 (1963); F. Varsanyi, Phys. Letters 11, 193 (1964).

[3] Visible or ultraviolet fluorescence lines terminating on these components have the same spectral resolution, but with the clean polarization lost and no information about the dynamic properties of the Y_1 levels at all.

[4] The full Nd^{3+} infrared double-resonance spectrum will be published in a more detailed paper.

[5] The same high-resolution 1.8-m Ebert spectrometer was used as for the double-resonance experiments, but the photomultiplier detector had to be changed to PbS, with a corresponding loss in both time response and sensitivity.

[6] One example is Er^{3+} in $LaCl_3$: F. Varsanyi and G. H. Dieke, J. Chem. Phys. 36, 2951 (1962). Here the ground-state components at 0, 37, 64, 96, and 114 cm^{-1} are sharp, while the higher ones are broad. Similar effects are rather commonly observed in many spectra.

[7] The term "metastable" is used here to designate a level with predominantly radiative decay and with emitted photons which can be detected.

[8] This difference is rather strongly demonstrated in the present system, where fluorescence from the X_1 level is intense at 4° but gradually weakens on raising the temperature and stops at about 17°K, and so does necessarily the quantum counter action. On the other hand, the Y_1 level is very well populated at 20°, and many of the double-resonance experiments were done at liquid-hydrogen temperature.

[9] While the present discussion centers on rare-earth levels in crystals, these are by no means the only possibilities for infrared double resonance.

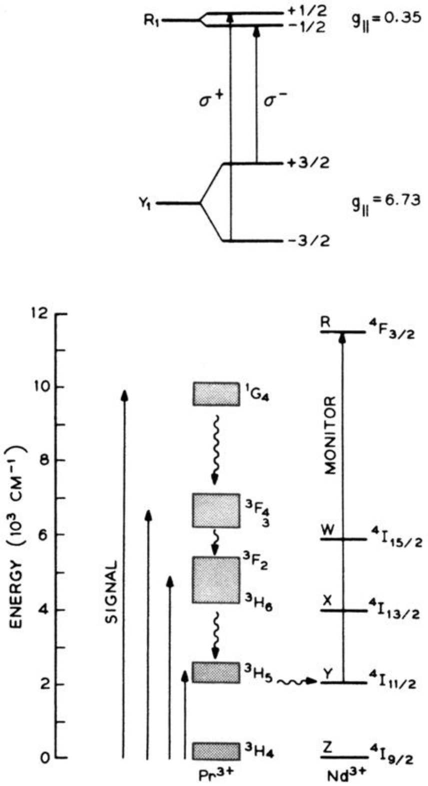
[10] It has been pointed out that the property of a quantum counter being noiseless is true in principle only if one does not include as part of the counter a final read-out device which will not be noiseless. It is generally assumed that a photomultiplier is to be used as a final detector. In this case, then, assuming that stray light has been eliminated completely, the limiting noise is the $\sqrt{n}$ noise due to the dark current of the phototube. While this is very small compared to the $\sqrt{n}$ noise in a monitor beam, it is not always negligible.

[11] In the present experiments about 2 μW of monitor energy reached the crystal, and a fraction of this was actually detected. Using the above assumption that the noise is limited by the statistical fluctuation of the monitor beam, and using the values of $f=5\times10^{-7}$ for oscillator strength, 0.1 cm^{-1} for linewidth of the Y_1-R_1 transition, and $\tau=0.1$ sec for lifetime of the Y_1 state, one obtains for minimum detectable number of ions $n_{\text{min}}=1.8\times10^{10}$, or a noise equivalent power $P_{\text{NE}}(5\ \mu)=7\times10^{-9}$ W for the Z_1-to-Y_1 infrared transition (equivalent to $D^*=1.4\times10^8$ in this case). This is about equal to the values of an uncooled PbSe detector at 4 μ. Assuming an infrared double-resonance detector using Ce^{3+} as the active ion with allowed electric dipole transitions to 5d states as the monitor transition (signal at 5 μ, $f=0.5$, linewidth 1000 cm^{-1}, $\tau=0.1$ sec), one obtains $D_{5\ \mu}^*=2.5\times10^{10}$. Comparison with existing far-infrared detectors is also interesting. Assuming again Ce^{3+} as the active ion for a 2000μ double-resonance detector (that is, the active level at 5 cm^{-1} and with a lifetime of 15 μsec), the detectivity is $D_{2000\ \mu}^*=1.4\times10^{10}$. The corresponding figure for a Golay cell is about 2×10^9, with 10 cps response, and for the carbon bolometer of Boyle and Rodgers, J. Opt. Soc. Am. 49, 66 (1959), it is $D^*=4.3\times10^{10}$ with a time constant of 0.01 sec.

[12] In the radio-frequency region the classic paper of A. Kastler, Physica 17, 191 (1951), and a more recent review article, A. Kastler, in Proceedings of the XIth Colloque Ampère, Eindhoven, 1962, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963), p. 14, are representative. In the microwave region, I. Wieder, Phys. Rev. Letters 3, 468 (1959), and the paper by C. K. Asawa and R. A. Satten, in Proceedings of the XIth Colloque Ampère, Eindhoven, 1962, edited by J. Smidt (Interscience Publishers, Inc., New York, 1963), p. 721, are related examples.

[13] While this process undoubtedly is a rather common loss mechanism, since it removes ions from the initial maser state, thus raising thresholds, relatively little attention has been paid to it. T. H. Maiman [Phys. Rev. Letters 4, 564 (1960)] suspected its presence in ruby under flash excitation, and A. Schawlow and co-workers [Bull. Am. Phys. Soc. 9, 706 (1964)] recently reported actual measurements, also in ruby.

[14] Such measurements on the present $PrCl_3(Nd^{3+})$ system are now being prepared. Transitions between the $+\frac{3}{2}$ and $-\frac{3}{2}$ components of the Y_1 neodymium level are forbidden in first order, and it is somewhat questionable whether sufficient intensity can be obtained here.



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