ION-PAIR RESONANCE MECHANISM OF ENERGY TRANSFER IN RARE EARTH CRYSTAL FLUORESCENCE

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Considerable detail about the interactions in a solid can be obtained if this solid has an absorption or fluorescence spectrum with sharp lines. As crystals with complicated structure present too many possibilities, we have endeavored to study the situation in relatively simple lattices and have found hexagonal $LaCl_3$ particularly useful, where the La^{3+} ions are partly or entirely replaced by a different rare earth ion.

These crystals show bright fluorescence from relatively stable levels of the ion. The behavior of the fluorescence spectrum when the crystal is illuminated by monochromatic radiation of changing frequency[1] presents a possibility of elucidating the fundamental processes which govern the transfer of energy within the crystal and the interaction between photons and crystal energy levels.

It appears that for the interpretation of some of the observed phenomena a cooperation of pairs of ions is necessary. The following experiment shows that one photon can excite two ions simultaneously.

When pure $PrCl_3$ is illuminated with light of frequency 20 475 cm^{-1}, the $^3P_0$ state is excited and fluorescence from this level is observed. The same fluorescence spectrum is observed when the frequency of excitation is changed so that higher electronic levels $^3P_1$, $^1I_6$, and $^3P_2$ are excited. The energy difference between these levels and $^3P_0$ is transferred to the lattice with a very short relaxation time. The full energy level diagram of $Pr^{3+}(4f^2)$ is shown on Fig. 1.

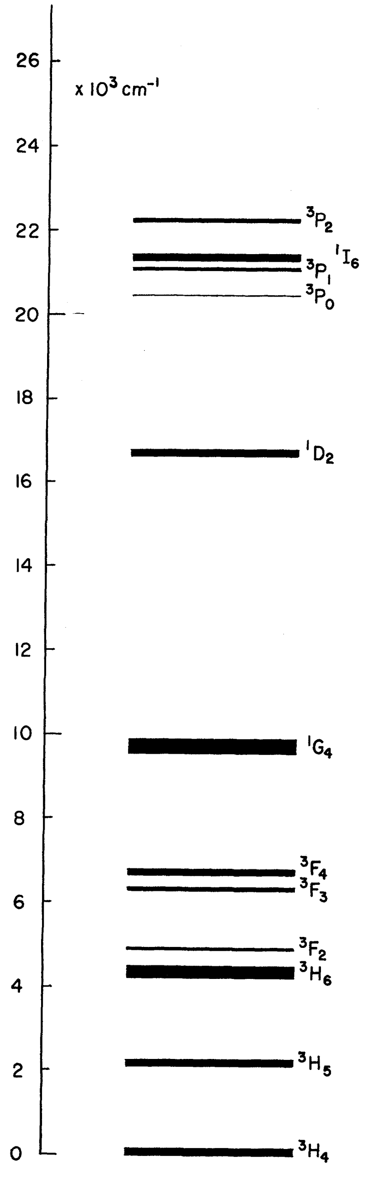

FIG. 1. Energy levels of $Pr^{3+}(4f^2)$. The width of the lines indicates the Stark splitting in a $LaCl_3$ crystal. The diagram is complete with the exception of one $^1S_0$ level which is predicted above 50 000 cm^{-1} by calculations.

The striking thing is that the same fluorescence spectrum is observed at definite excitation frequencies larger than that necessary to excite the $^3P_2$ state, in a region where it is definitely known that there cannot be any absorption lines of a single Pr^{3+} ion. A representative portion of the excitation survey plate is reproduced on Fig. 2. The frequencies where fluorescence is excited agree closely with frequencies necessary to excite simultaneously one Pr^{3+} ion to the $^3P_0$ state and a second ion to one of the lower excited states. This is shown by the following relations, where the number between parentheses shows the observed excitation frequency. All observed frequencies in this spectral region are included in the table and the agreement,

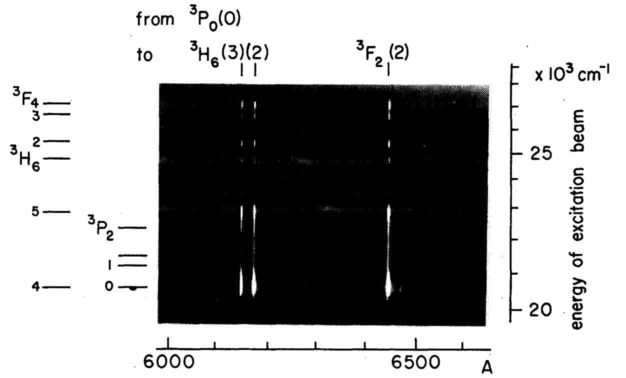

FIG. 2. Portion of the excitation survey plate taken at 4.2°K with a 100% $PrCl_3$ crystal. Any horizontal strip displays a fluorescence spectrum excited by the energy as marked on the right. Numbers in parentheses are the crystal quantum numbers of the respective Stark levels. Parts of two single-ion energy level diagrams are shown on the left to indicate the mechanism of excitation in a region with no single-ion levels.

$$\begin{aligned}
{}^3P_0+{}^3H_4 &= 20\,475+\quad 0=20\,475\ \mathrm{cm}^{-1}, \quad (20\,500)\\
{}^3P_0+{}^3H_5 &= 20\,475+2115=22\,590\ \mathrm{cm}^{-1}, \quad (22\,700)\\
{}^3P_0+{}^3H_6 &= 20\,475+4230=24\,705\ \mathrm{cm}^{-1}, \quad (24\,700)\\
{}^3P_0+{}^3F_2 &= 20\,475+4922=25\,397\ \mathrm{cm}^{-1}, \quad (25\,400)\\
{}^3P_0+{}^3F_3 &= 20\,475+6303=26\,778\ \mathrm{cm}^{-1}, \quad (26\,800)\\
{}^3P_0+{}^3F_4 &= 20\,475+6700=27\,175\ \mathrm{cm}^{-1}, \quad (27\,200)
\end{aligned}$$

is perfect within the limits of measurement.

The simultaneous excitation of two ions corresponds classically to the appearance of combination frequencies when two oscillators of different frequencies are linked by nonlinear forces sufficiently weak not to affect the frequencies seriously.

Optical phenomena which involve two or more crystal ions have been studied before. Schawlow, Wood, and Clogston[2] have explained the appearance of satellite lines in ruby as due to the resonance interaction of neighboring identical Cr^{3+} ions. Related are also the phenomena investigated in the field of sensitized luminescence[3] of phosphors.

The interaction of ion pairs also plays an important role in the dissipation of energy within the crystal. If a level X above a stable fluorescent level F is excited, fluorescence from F is observed and the difference $X-F$ is used for multiple phonon excitation. If $X-F$ becomes too large, the energy is not transferred directly from X to F and X becomes a stable fluorescent level. Our recent experiments have shown that if $X-F$ approaches the excitation energy of a low level of another ion, the transfer again takes place, that is to say fluorescence from F is again observed. The difference $X-F$ is then used to excite the second ion. In Er^{3+} this is found when X is approximately 6700 cm^{-1} above F. The energy of the first excited state is $Y = 6690\ cm^{-1}$.

In the classical picture this process corresponds to the emission of radiation of the difference frequency of two coupled oscillators with frequencies X and Y.

This type of ion-pair interaction in fluorescence has been observed throughout the whole rare earth series and explains some peculiarities of the observed fluorescence. For the lighter rare earths the lower states are relatively close together so that the regions of phonon and ion-pair interaction overlap. This means that generally there is cascading from the higher excited states to the lower ones and only relatively few fluorescent levels exist. For the heavier ions the lowest excited state is generally several thousand cm^{-1} above the ground state, which inhibits cascading in many cases. The experimental details will be given later.

The ion-pair resonance mechanism may play an important part in the optical pumping for maser materials. It has given rise to a number of questions which are now being studied experimentally. Effective optical pumping into infrared levels with ultraviolet light and without necessarily heating the lattice is accomplished in the Pr^{3+} case described above. The surplus energy is emitted in the visible. Similar processes involving dissimilar ion pairs are also possible.

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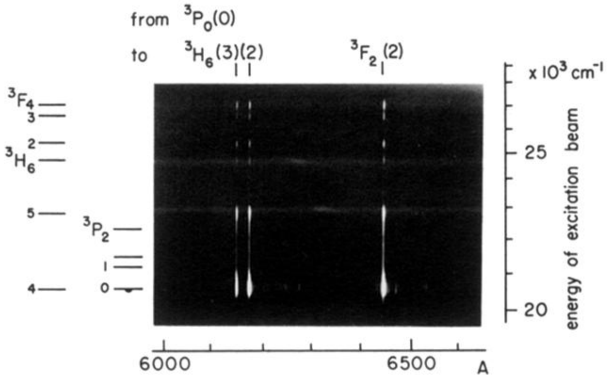
[1] F. Varsanyi and G. H. Dieke, J. Chem. Phys. 31, 1066 (1959).

[2] A. L. Schawlow, D. L. Wood, and A. M. Clogston, Phys. Rev. Letters 3, 271 (1959).

[3] D. L. Dexter, J. Chem. Phys. 21, 836 (1953); Phys. Rev. 108, 630 (1957); the first of these also contains many references.



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