Laser-induced fluorescence-line narrowing in ruby

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and $E(-+)$ is in fact a doublet, since one excites with $(+-)$ polarizations both $2p_{\pm1}(\Gamma_1+\Gamma_2)$ states, which are split in a magnetic field into $2p_{\pm1}\Gamma^-$ and $2p_{-1}\Gamma^+$ [$\Gamma^- = 2^{-1/2}(\Gamma_1 + i\Gamma_2)$, $\Gamma^+ = 2^{-1/2}(\Gamma_1 - i\Gamma_2)$]. Because of the resonance denominator in second-order perturbation theory, which describes two-photon absorption, with $(+-)$ polarizations one excites mainly the $2P_+\Gamma^-$ state (relative oscillator strength 1) and to a lesser extent the $2P_-\Gamma^+$ state (relative oscillator strength about $\frac{1}{4}$). For $(-+)$ light it is just the other way around. The difference in oscillator strengths between the $E(+-)$, $E(-+)$ and the $E(++)$, $E(--)$ bands can be explained by a two-band model[12] for the two-photon process. Taking the appropriate $1s\Gamma_5$ exciton as the intermediate state, one derives a factor of about 2 for the ratio of the different oscillator strengths $[f(--)/f(+-) \sim 2]$, which is well confirmed by the experiments.

In this Letter we have shown that two-photon magnetoabsorption is a powerful method to determine band parameters which could not yet be obtained by other experimental techniques. The accuracy of the results reported will be improved by detailed measurements of the field dependence, which should also yield information on diamagnetic shifts.

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LASER-INDUCED FLUORESCENCE-LINE NARROWING IN RUBY

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Using resonance ruby-laser excitation, narrowing of the ruby R_1 fluorescence line to width 0.002 cm^{-1} at 4.2°K is observed. Absence of spectral diffusion indicates that a short-range interaction rather than earlier postulated multipolar interactions is responsible for energy transfer in concentrated ruby.

A limiting factor in the resolution of sharp optical lines in gases and solids by conventional spectroscopy is inhomogeneous broadening. In gases, Doppler inhomogeneous broadening has recently been overcome by laser-saturated absorption[1] and fluorescent-line narrowing[2] resulting in the demonstration of ultrahigh-resolution spectroscopy at optical[3,4] and microwave frequencies.[5] For sharp zero-phonon lines in solids at low temperatures, the principal contribution to the linewidth arises from the inhomogeneous broadening effects of random strains caused by point defects or dislocations.[6] In this Letter we report, for the first time, the use of a laser technique to overcome inhomogeneous broadening in a solid. Cr^{3+} ions in a narrow frequency range are resonantly excited to the $^2E(\bar{E})$ level in ruby by a liquid-nitrogen–cooled ruby laser.[7] If the laser line is sufficiently sharp and spectral diffusion does not occur, the resulting fluorescence

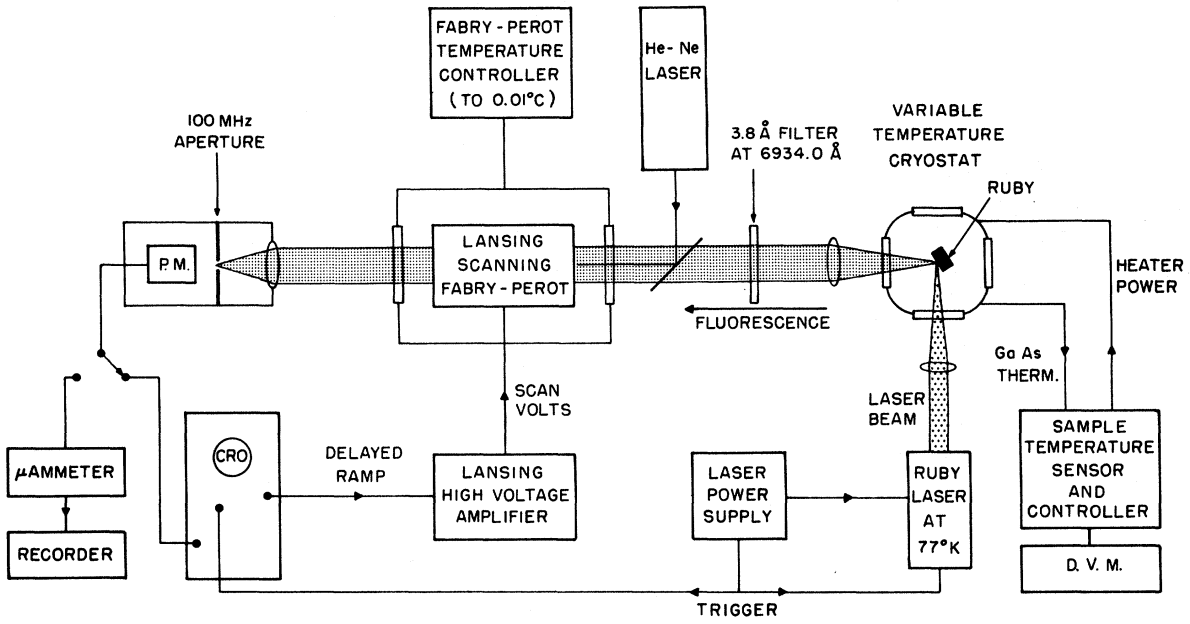

FIG. 1. Schematic of apparatus used for line-narrowing experiments.

linewidth is expected to be determined only by homogeneous broadening effects.

A schematic diagram of the apparatus is shown in Fig. 1. The laser ruby was immersed in liquid nitrogen and was flash-lamp pumped at an energy less than 0.5% above threshold to minimize sweeping of the laser frequency due to flash-lamp heating. The sample temperature could be varied over the range 4.2 to 300°K. A narrow-band filter was used to eliminate R_2 and phonon-assisted fluorescence. Following excitation of the transition $^4A_2(\pm\frac{1}{2}) \rightarrow \bar{E}$ by the $^4A_2(\pm\frac{3}{2}) \rightarrow \bar{E}$ laser line, the fluorescence spectrum was analyzed by the interferometer using a scan rate of 2 to 4 msec per order.

A high-resolution Fabry-Perot analysis of the R_1 fluorescence line using lamp excitation is shown in Fig. 2. The line shape is very closely a Gaussian indicating that the perturbations which broaden the line are random. The narrowest lines (2.2 GHz full width at half-maximum) were observed in a Czochralski ruby sample. For Verneuil rubies, inhomogeneous widths $\Delta\nu_i$ were broader, typically in the range 3.6 to 4.5 GHz at 4.2°K. The laser-induced fluorescent linewidth was independent of $\Delta\nu_i$.

A laser-excited fluorescent spectrum is shown in Fig. 3. The laser, which oscillates in two modes separated by 685 MHz, resonantly excites two groups of Cr^{3+} ions to the $\bar{E}$ level which then fluoresce to the doublet $^4A_2$ levels to give the observed four-line spectrum. The measured[8] linewidth of one component is 210 MHz which gives an intrinsic linewidth of 60 MHz if Lorentzian instrument (≃150-MHz width) and fluorescent line shapes are assumed. The amount of frequency drift in the laser is unknown; however, it may be noted that the observed linewidth is approaching the homogeneous linewidth of ≃10 MHz implied from photon-echo studies in zero magnetic

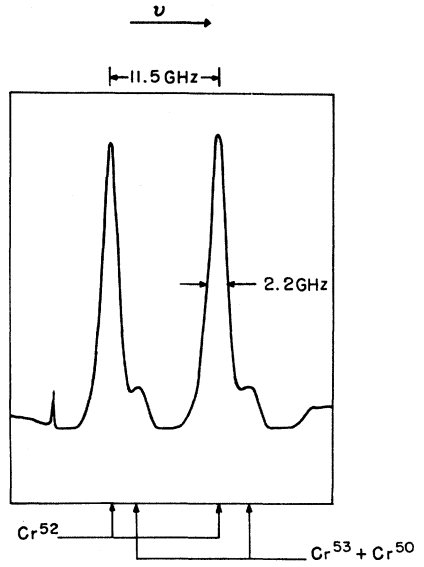

FIG. 2. Fabry-Perot analysis of tungsten-lamp–excited R_1 fluorescent spectrum of Czochralski ruby (0.05 wt% Cr_2O_3 at 4.2°K. Interorder separation of 11.5 GHz equals the R_1 splitting. The instrument linewidth is ~0.2 GHz.

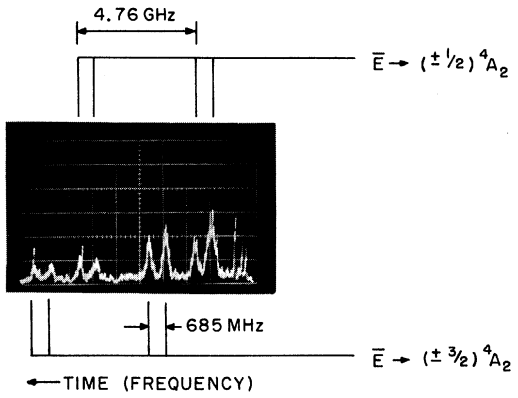

FIG. 3. Oscillogram of Fabry-Perot analyzed laser-induced fluorescence of the ruby R_1 line at 4.2°K. Sweep speed is 1 msec/cm.

field.[9]

An interesting aspect of the line-narrowing observations is that no spectral diffusion occurs over times of 10 msec which implies that single-ion–single-ion energy transfer is absent. As shown below, this observation is in conflict with the multipolar-interaction transfer mechanism recently proposed by Imbusch.[10] The probability per unit time for resonant energy transfer is given by

$$P = \hbar^{-2}\langle 1, 2^*|H_{\rm int}|1^*, 2\rangle^2 \int g_1(\nu) g_2(\nu) d\nu, \qquad (1)$$

where $|i\rangle$ and $|i^*\rangle$ are ground and excited states of atom i and $g(\nu)$ is the normalized line-shape function. For 1% ruby at 77°K, the experimental value[8] of 1 msec for single ion-pair transfer time gives $P \simeq 10^7$ sec^{-1} for single-ion–single-ion energy transfer.[11] If $H_{\rm int}$ is due to a quadrupole-quadrupole interaction, then the dependence of P on concentration C is given by

$$P \propto C^{10/3}/\Delta\nu_h \qquad (2)$$

for resonant energy transfer between ions with a homogeneous linewidth $\Delta\nu_h$. For 0.05% ruby at 4.2°K, we calculate $P \simeq 10^5$ sec^{-1}, where $\Delta\nu_h = 10^7$ sec^{-1} at 4.2°K and $\Delta\nu_h = 1.5 \times 10^9$ sec^{-1} at 77°K, the latter linewidth arising from phonon processes in ^2E. Such a fast transfer time in 0.05% ruby would clearly broaden the line appreciably over a time of 10 msec. In the latter calculation, we have assumed a macroscopic strain broadening in the sense that the ion resonant frequencies vary slowly with position in the crystal. If the other extreme of complete site-to-site randomness is assumed, then the transfer time increases by several orders of magnitude since adjacent ions are no longer "on speaking terms." A simple technique to overcome this is to raise the sample temperature until $\Delta\nu_h \simeq \Delta\nu_i$ giving $P \simeq 10^3$ sec. Experimentally no spectral diffusion was observed for temperatures up to 80°K. These results support Birgeneau's[11] calculations which show that multipolar interactions do not primarily determine energy transfer in 1% ruby but rather that the interaction must be of a short-range type such as direct exchange or superexchange.

In summary, it appears that the present technique could be applied to the high-resolution spectroscopy of zero-phonon lines in other solids using tunable dye lasers or parametric oscillators. Also applications are envisaged in studies of energy transfer, spectral diffusion, and elucidation of inhomogeneous broadening mechanisms in solids.

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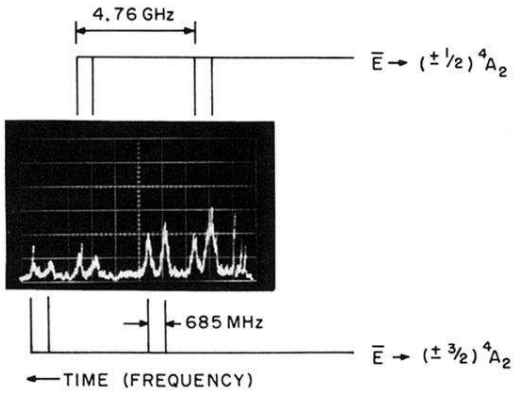

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