CONCENTRATION DEPENDENCE OF THE $\bar{E} \to 2\bar{A}$ FAR-INFRARED TRANSITION OF EXCITED CHROMIUM IONS IN RUBY

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The absorption due to electronic transitions between the excited $\bar{E}(^2E)$ state and the $2\bar{A}(^2E)$ state of Cr^{3+} ions in optically pumped ruby is studied by Zeeman spectroscopy with a far-infrared laser. We find that the linewidth and the oscillator strength of the $\bar{E} \to 2\bar{A}$ transition increase quadratically with the chromium concentration for ruby crystals containing more than 0.1 wt.% Cr_2O_3.

FAR-INFRARED electronic transitions of $3d$ ions in Al_2O_3 have been studied for a number of ions in their ground state [1, 2]. We report on a study of the electronic transition between the excited states $\bar{E}(^2E)$ and $2\bar{A}(^2E)$ of Cr^{3+} ions in Al_2O_3. We show that the linewidth and the oscillator strength of the transition are strongly dependent on the chromium concentration for ruby crystals containing more than 0.1 wt.% Cr_2O_3.

First informations on the linewidth of the $\bar{E} \to 2\bar{A}$ transition at low chromium concentration were obtained from experiments with high frequency acoustic phonons [3] and from optical detected magnetic resonance experiments [4]. These experiments have shown that the linewidth Γ of the $\bar{E} \to 2\bar{A}$ transition ($\simeq 0.02\,cm^{-1}$) is by two orders of magnitude smaller than the linewidths of far-infrared transitions of other $3d$ ions [1, 2] indicating that the $\bar{E} \to 2\bar{A}$ transition is only weakly influenced by crystalline fields. In this letter we report the first direct absorption measurement on this very narrow $\bar{E} \to 2\bar{A}$ absorption line and we show that chromium doping affects the transition very strongly.

The $\bar{E} \to 2\bar{A}$ transition in ruby has recently been of great interest with respect to detection, generation and trapping of high frequency phonons at $29\,cm^{-1}$ [5], and with respect to energy transfer processes [6]. It is therefore important to know the properties of the $\bar{E} \to 2\bar{A}$ transition.

In our experiment we used an HCN laser with emission at $29.7\,cm^{-1}$. The $\bar{E} \to 2\bar{A}$ transition (at $29.2\,cm^{-1}$) was tuned to the laser energy by the Zeeman effect. In a magnetic field applied parallel to the crystalline c-axis the Kramers levels $\bar{E}$ and $2\bar{A}$ split in doublets $\bar{E}_{\pm}$ and $2\bar{A}_{\pm}$ with the effective spin quantum numbers $\pm 1/2$. Resonance absorption is obtained at two magnetic fields corresponding to the transitions $\bar{E}_- \to 2\bar{A}_+$ and $\bar{E}_- \to 2\bar{A}_-$ (FIR in Fig. 1). The far-infrared laser radiation propagated along the c-axis and
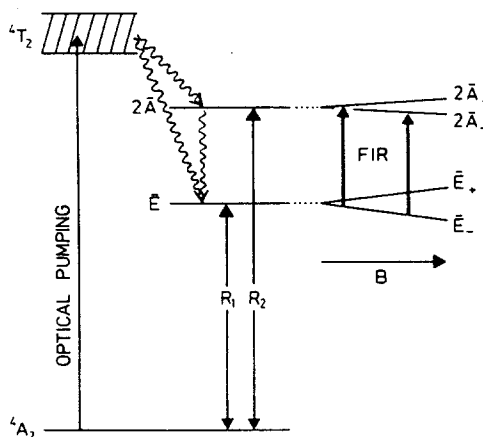

Fig. 1. Energy levels of Cr^{3+} ions in Ruby and splitting of the $\bar{E}$ and $2\bar{A}$ levels for a magnetic field B parallel to the c-axis.

was detected with a Golay cell. The crystal mounted in vacuum and cooled by mechanical contact to a temperature of 2 K was optically pumped with the radiation of a CW argon laser. By the optical pumping and fast relaxation the $\bar{E}_-$ and $\bar{E}_+$ states were populated. The optical pump radiation was chopped (with frequency 20 Hz) and therefore the populations of the $\bar{E}$-states (with lifetimes in the order of milliseconds) were modulated. The change of sample transmission caused by the optical pumping was detected by lock-in technique. The observed transmission change was in the order of a few per cent, therefore the lock-in signal is a direct measure of the $\bar{E} \to 2\bar{A}$ absorption induced by the optical pumping.

Experimental absorption curves are shown in Fig. 2 for the $\bar{E}_- \to 2\bar{A}_+$ transition. Resonance absorption occurs at a field strength of 0.5 T. The upper curve of Fig. 2 was obtained from a sample containing 0.05 wt.%
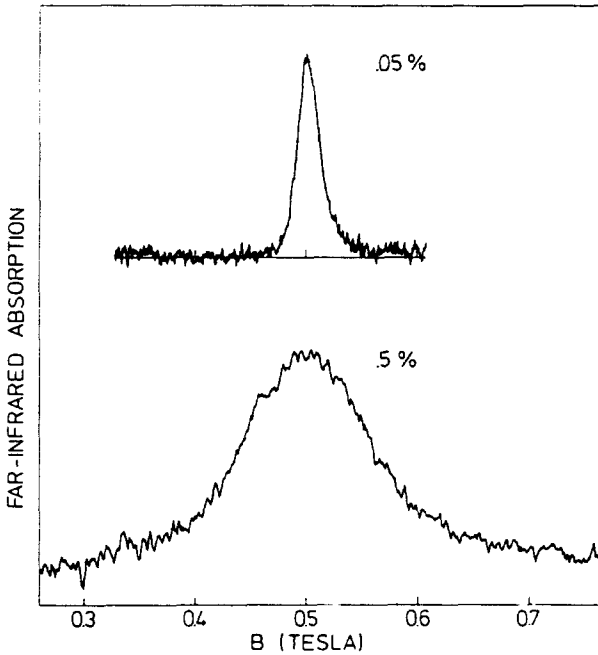
Fig. 2. Far-infrared absorption of optically pumped ruby due to $\bar{E}_- \to 2\bar{A}_+$ transitions for two samples with different chromium concentrations.

Fig. 3. Concentration dependence of the half-width Γ of the $\bar{E} \to 2\bar{A}$ absorption lines. The points are obtained from $\bar{E}_- \to 2\bar{A}_+$ and the circles from $\bar{E}_- \to 2\bar{A}_-$ absorption lines.

Cr_2O_3. The sample (thickness 1.5 mm, diameter 5 mm) was optically pumped in a diameter of 2 mm with an intense light beam (power about 2.5 W). From the absorption coefficient ($1\ cm^{-1}$) at the optical pump wavelength (514 nm) it is estimated that about 0.4 W optical power is absorbed in the crystal leading to a number of about $5 \times 10^{17}\ cm^{-3}$ Cr^{3+} ions in the $\bar{E}_-$ state. By comparing the signal intensity with the intensity of the far-infrared laser radiation reaching the Golay detector we estimated an absorption coefficient in the line maximum of about $0.2\ cm^{-1}$. As expected the absorption coefficient increased linearly with increasing population of Cr^{3+} ions in the excited $\bar{E}_-$ state in the range of our experiment ($0.5 \times 10^{17}\ cm^{-3}$–$1.5 \times 10^{18}\ cm^{-3}$) and, the linewidth of the resonance curve was independent of the optical pump intensity.

The lower curve of Fig. 2 was measured with a crystal containing a large concentration of Cr^{3+} ions (0.5 wt.% Cr_2O_3). The curve has been obtained with a crystal of 0.1 mm thickness (5 mm diameter) and an optical pumping laser power of 1.4 W. In the experiment with this sample a background signal was found indicating an additional absorption process independent of magnetic field. The linewidth of the absorption curve is about 5 times larger than the linewidth obtained for the diluted crystal. The absorption curves were found to be independent of sample temperature between 2 and 15 K. Therefore, the increase of linewidth with increasing concentration cannot be attributed to sample heating
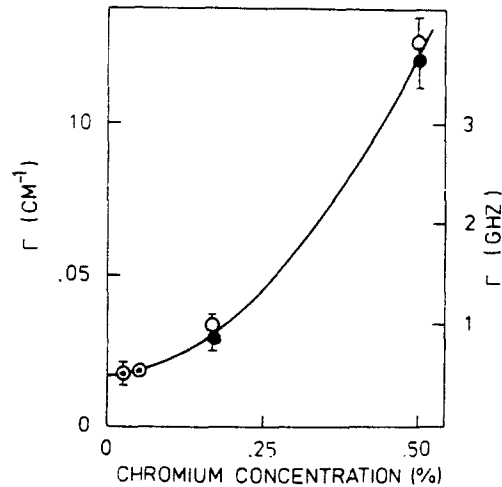
by the optical pumping which caused a temperature rise up to 6 K in the sample.

From the linewidths ΔB of the absorption curves (Fig. 2) the spectral linewidths Γ of the $\bar{E}_- \to 2\bar{A}_+$ transition are obtained according to the relation

$$\Gamma = \tfrac{1}{2}\mu_B(g_{\bar{E}} + g_{2\bar{A}})\Delta B \tag{1}$$

where $g_{\bar{E}} = 2.445$ [7] and $g_{2\bar{A}} = 1.47$ [8] are the g-values of the $\bar{E}$ and $2\bar{A}$ states for B parallel to c-axis and μ_B is Bohr's magneton.

Experimental results for the linewidth Γ (full width at half maximum) for samples with different concentrations of Cr_2O_3 are shown in Fig. 3. At low concentration the linewidth has a value of $\Delta B = 190$ G corresponding to $\Gamma_0 = 0.017\ cm^{-1}$ (520 MHz). It increases strongly at concentrations larger than about 0.1%. Writing the measured linewidth as a sum of two parts, $\Gamma = \Gamma_0 + \Gamma_c$, we find that the change Γ_c of the linewidth at higher concentrations increases quadratically with the concentration. A measurement on a sample containing 0.9 wt.% Cr_2O_3 confirms that Γ_c increases at least quadratically with concentration. The sample concentrations are those given by the crystal manufacturer [9].

We point out that our direct absorption experiment gives a width Γ_0 which is in agreement with the value obtained from a phonon experiment [3], but which is by a factor of 1.4 larger than the value observed in an optical detected magnetic resonance (ODMR) experiment. This is probably due to the fact that in the ODMR experiment line narrowing occurs due to phonon bottleneck effects.

We found that the $\bar{E}_- \to 2\bar{A}_+$ and $\bar{E}_- \to 2\bar{A}_-$ transitions have nearly equal oscillator strengths for the

far-infrared absorption. This indicates that we are dealing with electric rather than with magnetic dipole transitions. The $\bar{E} \rightarrow 2\bar{A}$ far-infrared transitions are only allowed due to the admixture of higher state wave functions to the $\bar{E}$ and $2\bar{A}$ state wave functions. There exist, however, no detailed calculations of far-infrared absorption as in case of phonon transitions between these states [10].

The absorption coefficient in the line maximum was approximately equal for the samples with different chromium concentrations, but at the same population density of chromium ions in the excited $\bar{E}_-$ state. This shows that the oscillator strength for the $\bar{E} \rightarrow 2\bar{A}$ far-infrared transition increases quadratically at high chromium concentrations. The position of the $\bar{E} \rightarrow 2\bar{A}$ absorption line was independent of the chromium concentration.

The origin of the line-broadening mechanism is not yet known. It is due to inhomogeneous broadening, as a homogeneous width of 5×10^{-3} cm^{-1} is expected according to a spin—lattice relaxation lifetime of 10^{-9} sec [11]. The quadratic dependence of Γ_c on the concentration gives some evidence that the linewidth is influenced by Cr^{3+} ion pairs the number of which is increasing quadratically with the Cr^{3+} concentration. Our results indicate that the chromium doping causes random electric or strain fields which lead to inhomogeneous line broadening as well as to an increase of the transition probabilities for $\bar{E} \rightarrow 2\bar{A}$ transitions.

It is interesting to compare our result with the concentration dependence of the $^4A_2 \rightarrow \bar{E}(^2E)$ transition. Optical absorption experiments [12] have shown that the widths and the positions of the R_1 and R_2 absorption lines are also influenced by chromium doping. For increasing chromium concentration both lines shift linearly to higher frequencies and the linewidths increase linearly, too. The increase has a value of about 1 cm^{-1} per % Cr_2O_3 in the range $c = 0.05 -$ 1.8 % Cr_2O_3. The oscillator strength of the optical transitions does not change with increasing chromium concentration. We therefore find that the $\bar{E}(^2E) \rightarrow 2\bar{A}(^2E)$ far-infrared transition is influenced by the doping in a very different way than the optical transitions from the ground state to the ^2E states.

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