

## HOMOGENEOUSLY BROADENED FAR-INFRARED ABSORPTION LINE DUE TO THE $\bar{E} \rightarrow 2\bar{A}$ TRANSITION OF EXCITED CHROMIUM IONS IN RUBY

N. RETZER, H. LENGFELLNER and K.F. RENK

*Institut für Angewandte Physik, Universität Regensburg, 8400 Regensburg, West Germany*

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By use of far-infrared laser spectroscopy, we have found that for a high-quality ruby crystal at low temperature, the absorption line due to the electronic transition between the excited states  $\bar{E}(^2E)$  and  $2\bar{A}(^2E)$  of  $\text{Cr}^{3+}$  ions is homogeneously broadened. From the linewidth ( $0.011 \text{ cm}^{-1}$ ) the lifetime of the  $2\bar{A}$  level against emission of  $29 \text{ cm}^{-1}$  phonons is obtained.

In this letter we show that for a high-quality ruby crystal at low temperature the far-infrared absorption line due to the electronic transition between the excited states  $\bar{E}(^2E)$  and  $2\bar{A}(^2E)$  of  $\text{Cr}^{3+}$  ions has almost lorentzian lineshape, and that the line is very sensitively influenced by strain fields. We will also discuss earlier studies of the  $\bar{E} \rightarrow 2\bar{A}$  transition, from which it was not clear, whether the  $\bar{E} \rightarrow 2\bar{A}$  absorption line is homogeneously or inhomogeneously broadened and which mechanisms are responsible for the broadening [1].

We point out that the excited states  $\bar{E}$  and  $2\bar{A}$  of  $\text{Cr}^{3+}$  ions in  $\text{Al}_2\text{O}_3$  play an important role in the field of phonon spectroscopy. Phonons at  $29 \text{ cm}^{-1}$  can be detected via  $\bar{E} \rightarrow 2\bar{A}$  transitions and generated by  $2\bar{A} \rightarrow \bar{E}$  relaxation processes. Resonance scattering due to phonon absorption and emission processes between the two levels can lead to spatial phonon trapping. For these studies it is very important to know the properties of the  $\bar{E} \rightarrow 2\bar{A}$  transition<sup>\*1</sup>.

The principle of our absorption experiment is shown in fig. 1. The  $\bar{E} \rightarrow 2\bar{A}$  transition (at an energy of  $29.2 \text{ cm}^{-1}$ ) was tuned to the emission frequency of a HCN laser ( $29.7 \text{ cm}^{-1}$ , bandwidth 10 MHz) by applying a magnetic field parallel to the crystalline c axis. The Kramers levels  $\bar{E}$  and  $2\bar{A}$  with the effective g factors  $g_{\bar{E}} = 2.445$  [3] and  $g_{2\bar{A}} = 1.47$  [4] split into

<sup>\*1</sup> For a survey see ref. [2].

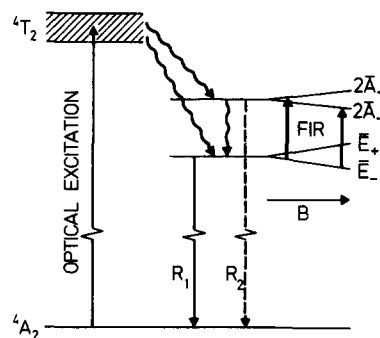


Fig. 1. Energy levels of  $\text{Cr}^{3+}$  ions in ruby in a magnetic field, showing the two possible far-infrared transitions  $\bar{E}_- \rightarrow 2\bar{A}_+$  and  $\bar{E}_- \rightarrow 2\bar{A}_-$  for fixed far-infrared laser frequency.

doublets  $\bar{E}_\pm$  and  $2\bar{A}_\pm$  with the effective spin quantum numbers  $\pm\frac{1}{2}$ . Resonance absorption is obtained at two magnetic fields (fig. 1) corresponding to the transitions  $\bar{E}_- \rightarrow 2\bar{A}_+$  and  $\bar{E}_- \rightarrow 2\bar{A}_-$ . The  $\bar{E}_\pm$  levels are populated by optical pumping into the  $^4T_2$  absorption band of ruby with radiation of an argon ion laser. Nonradiative decay leads to population of the  $\bar{E}_\pm$  levels. The argon laser beam was chopped with a modulation frequency (20 Hz) smaller than the decay rate (200 Hz) of the population of the  $\bar{E}$  levels which decay by fluorescence. Therefore, the optical pumping leads to a modulation of the far-infrared absorption.

The ruby crystal was located in the field of a superconducting magnet with the c axis parallel to the mag-

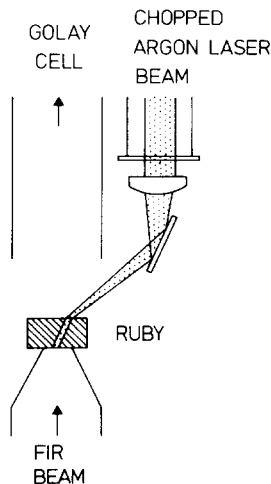


Fig. 2. Experimental arrangement.

netic field. To achieve effective cooling the crystal ( $6 \times 6 \times 4 \text{ mm}^3$ ) was surrounded by superfluid helium at 1.8 K. The optical configuration is shown in fig. 2. A small part of the sample was irradiated with a focused argon laser beam (wavelength 514.5 nm, power 1 W). The optically pumped small cylinder (diameter 0.4 mm) was oblique (with an angle of  $25^\circ$ ) to the crystal  $c$  axis. In order to avoid deflections by an undulating free surface of the liquid helium the argon laser beam was brought into the cryostat by a vacuum chamber that had windows plunged in the liquid helium. Far-infrared laser radiation was focused by a cone on the crystal and transmitted by a metal tube to a Golay detector. The detector signal, analysed by a lock-in technique, was a direct measure for the optically induced far infrared absorption. With our arrangement it was possible to obtain sufficient cooling of the sample and also to avoid modulation of the far-infrared radiation by fluctuations in the liquid helium due to bubbles generated by the strong optical radiation. We have performed our experiment with a crystal<sup>‡2</sup> containing 0.05 wt%  $\text{Cr}_2\text{O}_3$ .

An experimental absorption curve for the  $\bar{E}_- \rightarrow 2\bar{A}_-$  transition is drawn in fig. 3. Resonance absorption occurs at a field of  $B = 2.2 \text{ T}$ . A comparison of the experimental curve with a lorentzian line profile (dashed line in fig. 3) and with a gaussian profile (dotted) shows

<sup>‡2</sup> Delivered by Hrand Djevahirdjian Ltd., Monthey/Switzerland.

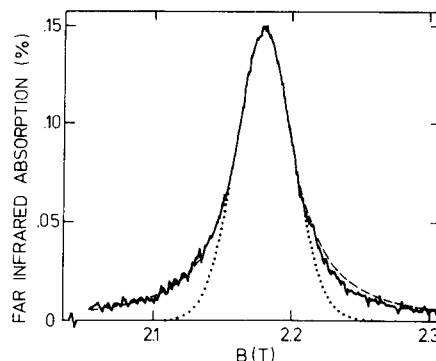


Fig. 3. Far-infrared absorption line due to the  $\bar{E}_- \rightarrow 2\bar{A}_-$  transition of excited  $\text{Cr}^{3+}$  ions in ruby. Lorentzian and gaussian line profiles are shown for comparison.

that the absorption curve can be described by a lorentzian, but not by a gaussian profile. This indicates that the line broadening is mainly due to homogeneous broadening. The halfwidth (full width at half maximum) is  $\Delta B = 49.0 \times 10^{-3} \text{ T}$ . According to the relation

$$\Delta\nu = \frac{1}{2}(g_{\bar{E}_-} - g_{2\bar{A}_-})\Delta B\mu_B/h, \quad (1)$$

where  $\mu_B$  is Bohr's magneton and  $h$  Planck's constant we obtain a homogeneous linewidth of  $\Delta\nu = 334 \text{ MHz}$ . The homogeneous width could be slightly smaller (by 10%), since the profile of the measured absorption curve could also be described by a Voigt profile [5] with a slightly smaller homogeneous width (300 MHz) and an inhomogeneous width (100 MHz) which is less than a third of the homogeneous width. We note that the linewidth was not dependent on the concentration of excited chromium ions, which we have varied by two orders of magnitude (between  $10^{16} \text{ cm}^{-3}$  and  $10^{18} \text{ cm}^{-3}$ ).

We found that the absorption curve due to the  $\bar{E}_- \rightarrow 2\bar{A}_+$  transition has almost the same oscillator strength as the  $\bar{E}_- \rightarrow 2\bar{A}_-$  transition and that lineshape and linewidth (in the frequency scale) were the same. This result indicates that the  $\bar{E} \rightarrow 2\bar{A}$  far infrared transitions are electric dipole transitions rather than magnetic dipole transitions in which case different oscillator strengths would be expected. The excited state absorption is very weak. The change of sample transmission in the line maximum at a concentration of  $1.5 \times 10^{17} \text{ cm}^{-3}$  chromium ions was about 0.15% (fig. 3). We estimate from experiments with different geometries of the optically excited volume that the cross section for

the  $\bar{E} \rightarrow 2\bar{A}$  far-infrared transition in the line maximum is about  $3 \times 10^{-19} \text{ cm}^2$ .

From the homogeneous linewidth we obtain a lifetime of the  $2\bar{A}$  level of  $T_1 = (2\pi\Delta\nu)^{-1} = 4.8 \times 10^{-10} \text{ s}$  ( $\pm 10\%$ ). This value is in very good agreement with a value derived recently from the temperature-dependent line broadening of the  $\bar{E} \rightarrow 2\bar{A}$  absorption line [6] and is also in good agreement with the theoretical prediction ( $3 \times 10^{-10} \text{ s}$ ) [7]. The value of  $T_1$  is by a factor of two smaller than concluded from a time-resolved fluorescence experiment [8].

The decay of the  $2\bar{A}$  states is mainly due to non-spin-flip transitions ( $2\bar{A}_- \rightarrow \bar{E}_-$  and  $2\bar{A}_+ \rightarrow \bar{E}_+$  respectively). The lifetime  $T_{+-}$  ( $1.5 \times 10^{-8} \text{ s}$ ) for spin-flip transitions is known from a study of Orbach spin-lattice relaxation of the  $E_+$  state which occurs via  $2\bar{A}$  states [9]. It follows therefore that the relaxation time  $T_{++}$  for non-spin-flip transitions is  $T_{++} = T_1 T_{+-} / (T_{+-} - T_1)^{-1} = 5.0 \times 10^{-10} \text{ s}$  ( $\pm 10\%$ ) and that the non-spin-flip transition occurs 30 times faster than the spin-flip transition.

The lorentzian lineshape and the narrow linewidth were only obtained for high-quality samples. We found that various effects can influence the linewidth. Inhomogeneous stress obtained by fixing the crystal too strongly in the sample mount already leads to additional line broadening and to a change of the line profile. We found that, for an unstrained crystal, the resonance frequency for the  $\bar{E} \rightarrow 2\bar{A}$  transition depended slightly on the region within the crystal, and that in an arrangement with homogeneous sample illumination instead of illumination with a focused beam, the line was broader and the lineshape non-lorentzian. Our observation indicates therefore that macroscopic strain inhomogeneities in the crystal cause locally slightly different resonance frequencies for the  $\bar{E} \rightarrow 2\bar{A}$  transitions. Inhomogeneities have recently also been observed by analysis of the optical transition from the ground state  $^4A_2$  to the  $\bar{E}$  state [10].

The results shown in fig. 3 were obtained for a Czochralski grown crystal. Verneuil crystals containing low concentrations of  $\text{Cr}_2\text{O}_3$  have a  $\bar{E} \rightarrow 2\bar{A}$  far infrared absorption line which is by a factor of two larger ( $\Delta\nu = 0.020 \text{ cm}^{-1}$ ) than for the Czochralski crystal. The larger linewidth is due to inhomogeneous broadening, while the homogeneous contribution is the same as in the Czochralski crystal as has been concluded from the temperature dependence of the linewidth [6]. We

found that in Verneuil crystals the  $\bar{E} \rightarrow 2\bar{A}$  resonance frequency can vary over small distances within the crystal by as much as one linewidth.

A further strong influence on the  $\bar{E} \rightarrow 2\bar{A}$  transition is obtained by increasing the  $\text{Cr}_2\text{O}_3$  concentration. As has been shown (for Verneuil crystals) the linewidth of the  $\bar{E} \rightarrow 2\bar{A}$  transitions increases strongly at concentration larger than 0.1 wt%  $\text{Cr}_2\text{O}_3$  [1]. Probably, internal strain fields are introduced by the doping.

We note that in an earlier experiment the  $\bar{E} \rightarrow 2\bar{A}$  far-infrared absorption was detected indirectly by far-infrared induced  $R_2$  fluorescence. From this optically detected magnetic resonance experiment performed for a Verneuil crystal a linewidth was concluded to the value found for the high quality crystal. However, the agreement is accidental because in the optically detected magnetic resonance experiment phonon trapping effects lead to an apparent line narrowing. An analysis of the experiment, which takes into account trapping effects, leads also to a value of the linewidth ( $0.02 \text{ cm}^{-1}$ ) which agrees with the absorption experiment on this crystal [6]. We point out that linewidths were also derived from experiments with  $29 \text{ cm}^{-1}$  phonons using various techniques of phonon spectroscopy [11,13]. The analysis of these experiments performed on Verneuil crystals of various sources leads also to the linewidth ( $0.02 \text{ cm}^{-1}$ ) typical for the Verneuil crystals.

To our knowledge the  $\bar{E} \rightarrow 2\bar{A}$  absorption line in a high-quality crystal is the narrowest homogeneously broadened absorption line in a crystal at low temperature. The broadening is only due to the lifetime of the  $2\bar{A}$  level against emission of  $29 \text{ cm}^{-1}$  phonons. The system is therefore most suitable for the study of the resonance interaction of high-frequency phonons with an electronic two-level system and for effective generation and detection of phonons.

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