

Time-resolved photo-phonon spectroscopy of exchange coupled Cr^{3+} – pairs in ruby

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A rather simple method is used to detect at once both optical absorption spectra and excited-states nonradiative transitions in 0.03 at.% and 0.16 at.% ruby at temperature 2 K. The technique utilizes a time-resolved bolometer detection of phonons, generated by the excited-state nonradiative relaxation following optical excitation with a pulsed tunable dye laser. The observed excitation spectra of phonons well coincide with already known absorption spectra of both single chromium ions and pairs of the nearest neighbors. For the first time the fast ($\leq 0,5 \mu\text{s}$) resonant energy transfer from single chromium ions to the fourth-nearest neighbors is observed directly. The new strongly perturbed Cr-single-ion sites are observed.

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The used method can be referred, as photo-phonon spectroscopy. The nonequilibrium phonons, which are created after laser pulse excitation due to radiationless relaxation, can be detected as bolometer temperature changing in real time following laser excitation, if a free length of the phonons is comparable to distance up to a bolometer. Therefore, the bolometer signal amplitude is determined by both the absorption cross section and the radiationless relaxation intensity so both absorption spectra and radiationless relaxation can be studied by this method. For the first time this technique was proposed in [1]. It is a natural development of the photo-acoustic [2] method. Absorption spectra of ruby in the $R_1 - R_2$ region were observed in [1] utilizing sinusoidally chopped light excitation. We use a pulse laser excitation and wider rang of the light wave lengths then in [1]. It has allowed us to identify the lines of chromium ion pair and to deduct about the fast resonant energy transfer from single ions to the fourth nearest neighbors and about new single ion sites.

The geometry of experiment is shown in Fig.1. The dye (oxazin 1) tunable laser is used for optical excitation of Cr^{3+} ions. It produces light pulses of 8 ns in duration with a repetition frequency 12.5 Hz and a spectral half-width 0.1 \AA at any wave length in the range $6915 \text{ \AA} \div 7100 \text{ \AA}$. The samples of a ruby have Cr^{3+} concentration 0.03 at.% and 0.16 at.% and thickness (along axis C_3) 10.0 mm and 5.0 mm accordingly. Linearly polarized laser radiation is transmitted through a sample along the C_3 -axis. The phonon pulse created at passage of laser radiation through a sample are detected by a superconductive Sn- or In-bolometer. The bolometer

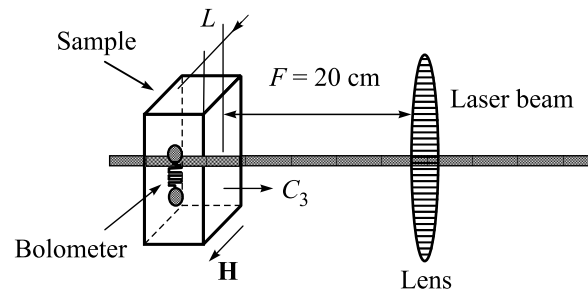


Fig.1. The experimental geometry. \mathbf{H} and C_3 – directions of an exterior constant magnetic field and an optical axis, L – the distance between a laser beam and a bolometer (it is fixed in our experiments), F – focal distance

was evaporated on one of lateral sides of a sample. It's shape is a meander and area 3 mm^2 . Samples are immersed in liquid helium which is pumped down to 2 K. The working point of a bolometer is tuned to the inferior part of the linear site of superconductive transition due to an external magnetic field. The bolometer signals are amplified using a wide-band preamp with a small noise signal. Data output is via stroboscopic oscilloscope. All processes of measuring (detecting of a signal, its accumulation and processing, change of a wave length of the laser) were automated.

It is necessary to note, that the laser wave length can be changed with a step, smaller 0.005 \AA , however the reflecting monochromator, used by us, did not allow to establish the wave length values with this accuracy. Precisely enough it was possible to establish only the wave length relative change. Besides in the literature there is no unambiguity in wave length values of the R_1 and R_2 lines of a ruby. Though some authors give its to within the 0.01 \AA , the wave length value, for exam-

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ple, R_1 lines at helium temperature in different works varies from 6933.6 Å to 6935.0 Å [3–5]. Therefore, in order to prevent confusion at identification of lines, we further considered, as well as in [3] where the complete data on absorption spectra and luminescence of the concentrated ruby are cited most, $\nu(R_1) = 14418.52 \text{ cm}^{-1}$, i.e., $\lambda(R_1) = 6933.6 \text{ Å}$.

When a sample is excited by a laser pulse, the bolometer detects a phonon pulse after some delay time depending on the distance L between the impact laser point and the bolometer ($L = 2.5 \text{ mm}$ for results, shown in Figs.1–6).

Typical signals are shown in Fig.2. The spike at the time initial moment in this figure is because the bolome-

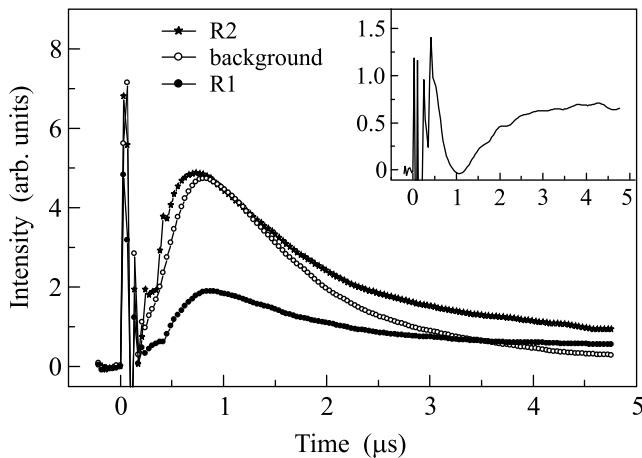


Fig.2. Bolometer signals in the ruby (0.16 at.% Cr^{3+}) versus the time after the laser pulse excitation: Background - nonresonance excitation ($\lambda = 6922 \text{ Å}$), R_1 and R_2 - resonance excitation of the R_1 and R_2 lines. The inset shows the difference between the R_2 and background phonon signals. Time - is delay time after the laser pulse excitation

ter detects not only phonons, but also the light scattered in the sample. The phonon pulses were observed at all the explored laser wave length band, i.e., that is also and at nonresonance laser excitation, which light frequency was differed from frequencies of optical transitions both single ions as pairs of the nearest neighbors. The reason of nonresonance laser generation of these background phonons is not clear and demands separate studying. During wave length scanning the amplitude of a bolometer signal is measured at some fixed delay time after the laser pulse excitation. The number of accumulation in each point is equal 50. Then the specter is normed on the background, because the dye laser pulse intensity depends on wave length. Further, everywhere,

where we shall speak about a phonon excitation specter, the specter received thus will be meant.

At scanning of a wave length of the laser in a low concentrated ruby we observed change of the phonon signal only in the vicinity of the R_1 and R_2 lines (see Fig.3).

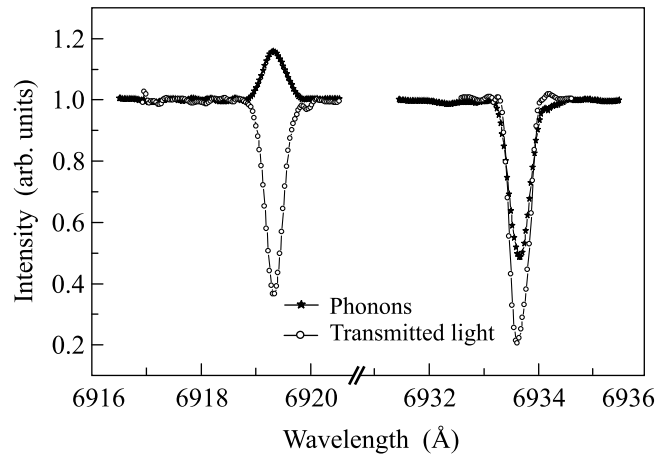


Fig.3. Transmissivity and phonon excitation spectra near the R_1 and R_2 lines in the low concentrated ruby sample (0.03 at.% Cr^{3+})

As you can see from this figure, the considerable decreasing of the phonon signal is observed at resonant pumping of R_1 line. Probably, it is caused by decreasing of background phonons generation due to absorption of a laser pulse in volume of the sample, giving to decreasing of the laser pulse intensity. Growth of the phonon signal at the resonance with a R_2 line may be explained by creation of additional 29 cm^{-1} phonons generated by the excited-state nonradiative relaxation $2\bar{A} \rightarrow \bar{E}$ as in [6].

The most interesting results were received in the concentrated ruby sample (0.16 at.% Cr^{3+}). In our work the transmission spectrum was measured without use of a monochromator. The wave length of the input laser is varied. The output laser pulse, past through a sample, is detected by a photomultiplier. Rather low peak stability of dye laser pulses, plus usage of the high-speed photomultiplier, importing additional noise, and also is essential a smaller chromium ion concentration gave to that in a transmission spectrum only R_1 and R_2 lines were well observed as you can see in Fig.3. However, when we begin to detect phonon signal on a bolometer, but not a transmission specter, we have received unexpected interesting results (see Fig.4). There is addition generation of phonons at particular excitation wave lengths.

In Fig.4 all known absorption lines of chromium single ions and pairs of the nearest neighbors are shown

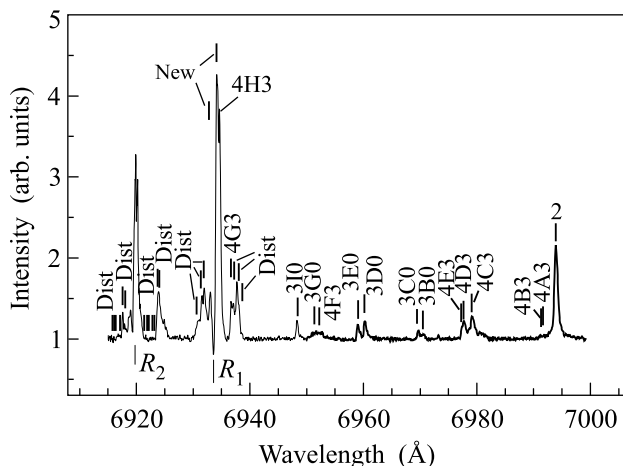


Fig.4. Phonon excitation spectra at $3 \mu\text{s}$ delay time after the laser pulse in 0.16 at.% Cr^{3+} ruby at temperature 2K versus on the laser wave length. The lines show locations of the all absorption lines at the region $6915 \text{ \AA} \div 7000 \text{ \AA}$ found in [3] for temperature 4 K and polarization $\mathbf{E} \perp C_3$. Labels as in [3]. The line $4H3$ is not mentioned in [3], the line $4F3$ is mentioned in [3], but the transition frequency value is not given so these values are accepted equal to the calculated values given in [3]: $\nu(4H3) = 14416.2 \text{ cm}^{-1}$ and $\nu(4F3) = 14379.9 \text{ cm}^{-1}$. The value of frequency of transition $4G3$ is given as in [3] for polarization $\mathbf{E} \parallel C_3$

also. In view of that spectral width of the laser in our experiment about 0.1 \AA , coincidence of the experimental values of lengths of waves, at excitation on which is observed change of phonon signal, to absorption lines of the nearest neighbors is quite satisfactory. It is visible, that the lines, excitation of which is not accompanying with nonradiative transitions ($4A3$, $4B3$), are not observed by the method utilized in the given work. Therefore, it is possible to count, that change of the phonon signal is bound to generation of phonons due to nonradiative transitions from optical excited state on a metastable level.

Let's consider more in details the phonon excited spectra in area R_1 and R_2 lines. As you can see in the inset of Fig.2, R_2 -excited phonon signal differs under the shape from a background phonon signal and has the expressed ballistic character. Indeed, at short times equal the times of flight of ballistic longitudinal and transverse 29 cm^{-1} phonons, the bolometer signal amplitude has peaks. The excitation wave lengths of these phonons peaks are near the transmissivity dip ($\lambda = 6919.26 \text{ \AA}$), as you can see in Fig.5. At increasing of a delay time, these peaks decrease and two new excitation lines of phonons with $\lambda = 6919.85 \text{ \AA}$ and $\lambda = 6920.17 \text{ \AA}$ become visible in the phonon excitation spectra. These lines are in longwave area of R_2 region.

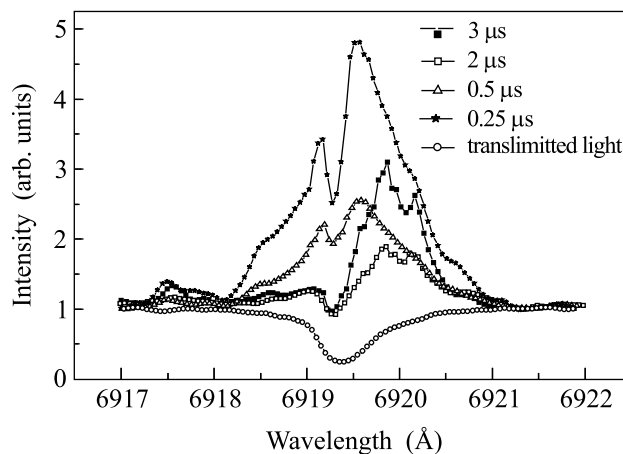


Fig.5. R_2 -region of the laser pulse transmissivity and the phonon excitation spectra of the Fig.4 at the different delay times after the laser pulse input

Even more interesting situation is observed in the R_1 region, as you can see in Fig.6. Already at small delay times about $0.5 \mu\text{s}$ there is well allowed line lower than

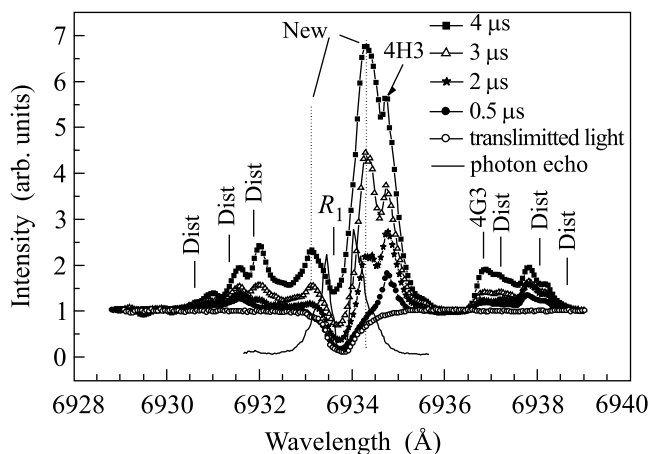


Fig.6. R_1 -region of the phonon excitation spectra of Fig.4 at the different delay times after the laser pulse input. Also the laser pulse transmissivity and amplitude of the backward two pulse (delay time 30.0 ns between the pulses) photon echo near the R_1 line are shown

a R_1 -level on 1.1 \AA in the phonon excitation specter. It is known, that approximately here there should be the line of the fourth nearest neighbors $4H3$ which is very difficult to resolve by direct optical methods: the energy level experimental value is not given in [3], $\nu(4H3) = 14416.7 \text{ cm}^{-1}$ [7, 8], $\nu(4H3) = \nu(R_1) - 2.0 \text{ cm}^{-1}$ [9] that is $\nu(4H3) = 14416.52 \text{ cm}^{-1}$. Just approximately in this place ($\nu = 14416.36 \text{ cm}^{-1}$, $\lambda = 6934.65 \text{ \AA}$.) the peak in the phonon excitation spectra is observed at all delay times, as you can see in Fig.4 and Fig.6. Presence or

absence of the line located on frequency is little bit lower than R_1 -line, it is very important [9, 8, 10] for examination of mechanisms of migration of energy from single ions to pairs. However intensities of phonon signals on transitions $4H3$ and $4G3$ pairs are expected equal [8], and in our experiment strongly differ. Probably, it is so because at the $4H3$ -transition frequency simultaneously with pairs the single ions are excited, which fastly transfer energy to ones. It is possible to tell, that for the first time the fast resonance transfer of energy from single ions to pairs of the fourth-nearest neighbors has been detected directly.

At last, you can see in Fig.4 and Fig.6, that at increasing of a delay time two new lines become visible in the phonon excitation spectra. One of them ($\lambda = 6933.11 \text{ \AA}$) is some more to the up of the R_1 line, and another, very intensive ($\lambda = 6934.3 \text{ \AA}$) is some more to the down. From the different literary data follows, that the level $4I3$ or practically coincides with R_1 -line [3], or lays above on 0.5 cm^{-1} [7, 8]. At us the difference between $\lambda = 6933.11 \text{ \AA}$ and R_1 lines is almost 1.0 cm^{-1} . Besides, as against $4G3$ and $4H3$ lines, this line is not observed at $0.5 \mu\text{s}$ delay time. Therefore for the statement, that is the line of pairs $4I3$ there are no major bases. The not clearest is occurrence of phonon peak with $\lambda = 6934.3 \text{ \AA}$. At delay times less than $1.0 \mu\text{s}$ it is not observed at all, and then very fast grows with increasing of delay time, i.e., there is an effective phonon generation delayed in time at this wave length. As the time dependence of this phonon peak sharply differs from ones of $4G3$ and $4H3$ (and also the third and distant neighbors) we count, that this line originate from strongly perturbed Cr single ions, near to but not part of pairs. Indirect confirmation of this conclusion is that almost on the same distance from a R_2 line the phonon peak (see Fig.5) also is observed. As you can see in this Figure the dip in the backward photon echo amplitude is by to the strong resonant absorption of the second laser pulse, twice past through a sample. It is visible, that the pairs $4H3$ does not render practically any influence on a photon echo signal. Against this some influence of new centers with $\lambda = 6933.13 \text{ \AA}$ and $\lambda = 6934.3 \text{ \AA}$ affecting on the photon echo signal shape of uprise and wane versus wave length. It, in our opinion, again testifies for the benefit of that these two lines belong to single chromium ions. Qualitatively similar to our phonon excitation spectrums the spectra of fluorescence excitation were observed in [11] at $5.0 \mu\text{s}$ delay in 0.51 at. % ruby at 6 K in the region of the $R_1 - R_2$ lines. It was assumed in [11], that the new lines of fluorescence excitation in

vicinity of the R lines, are originate from R' ions. These ions [11] are neither truly isolated nor tightly bound into triplet and they couple strongly to the pair but only weakly to the isolated R ions. In [11] the lines similar to 6920.17 \AA and 6934.13 \AA were concerned to N_2 -excitation lines, and similar to 6933.13 \AA was concerned to N_1 -excitation line.

Thus, it is shown, that the time-resolved photo-phonon spectroscopy appears very sensing method of detection of optical transitions in those excited states which have the strong nonradiative relaxation. A time resolution of the method is defined by a bolometer rise-time (it is about 30.0 ns in the case of the In-bolometer and 20.0 ns in the case of the Sn-bolometer) and allows to observe the spectra evolution on a nanosecond time scale. A combination of this method and detection of the time-resolved fluorescence excitation spectra give more the complete physical pattern of such phenomena, as, for example, process of energy transfer between single ions and pairs of the nearest neighbors, so up to the end not solved to this day, by that there are all new and new models [12] at this problem.

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