

Nonresonant interaction between phonons with a transition between the components of the 2E doublet of a chromium ion in ruby

A. P. Abramov, I. N. Abramova, I. Ya. Gerlovin, and I. K. Razumova

(Submitted 11 July 1979; resubmitted 5 January 1980)
Zh. Eksp. Teor. Fiz. 79, 1303-1308 (October 1980)

A dependence of the waveform of the pulse from a ruby optical phonon detector on the temperature of a pulsed source of nonequilibrium phonons has been observed. It is concluded on the basis of the experimental results that, the prevailing opinions notwithstanding, much of the phonon-detector signal is produced by phonons that are not at resonance with the transition between the components of the 2E doublet of the chromium ion, but by phonons with energy 29 cm^{-1} higher than the splitting energy. The signal fraction due to the resonant phonons, and hence the degree of selectivity of the phonon detector, depends on the experimental condition, in particular on the concentration of the excited chromium ions in the detecting volume. It is shown that at high concentrations ($\sim 10^{16}\text{ cm}^{-3}$) and at high temperatures of the pulsed heater the main contribution to the signal is made by the nonresonant phonons.

PACS numbers: 63.20. — e

The interpretation of the experiments on fluorescent detection of phonons¹⁻⁴ is based on the concept of resonant excitation of phonons, with an impurity center serving as the detector. In such experiments the presence of nonequilibrium phonons in a cooled crystal is revealed by determining the population of the upper component of the split electronic state of the impurity center. At the same time, as is known from experiments on spin-lattice relaxation,⁵ the populations of the electronic state can change not only as a result of the resonant (direct) absorption of phonons, but also on account of absorption of high-energy phonons with emission of difference-frequency phonons (a Raman-effect process). In the Terahertz frequency region, which is the important one in the experiments on fluorescent detection, the cross section of the resonant absorption exceeds by several decades the cross section of the Raman process. The cross-section difference, however, can be offset by the much larger width of the spectrum of the Raman phonons, since resonant absorption is possible only within the limits of the contour of the electronic transition, whereas the frequency band of the phonons that interact nonresonantly with the center is of the order of the transition frequency. Nonresonant interaction with phonons can thus turn out to be substantial under certain conditions not only in EPR spectroscopy but also in experiments on fluorescent detection. In the present communication we report the results of research aimed at observing nonresonant interaction of phonons in the Terahertz band with the electronic states of the chromium ion in ruby.

Phonons in ruby are detected by using the transition between the components $2\bar{A}$ and \bar{E} of the lowest excited state 2E of the chromium ion. The splitting amounts to 20 cm^{-1} (0.87 THz). The nonequilibrium phonons are usually generated by pulsed heating of a constantan film sputtered on the surface of the crystal, and the role of the detector is played by a small volume excited by continuous irradiation. The population of the upper component of the doublet is fixed from the appearance in the luminescence spectrum of the crystal cooled to 2 K , of

the R_2 line due to the $2\bar{A}({}^2E) \rightarrow {}^4A_2$ transition.

In the present study the luminescence was excited by light passing from a DRS-500 lamp through a rectangular diaphragm that was projected on the sample in the form of a strip 0.3 mm wide (Fig. 1d). The procedure used to generate the thermal pulses and to register the signal did not differ from that described in Ref. 2. A distinguishing feature of the experiments considered here was the variation of the amplitude of the electric pulses applied to the heater, i. e., of the phonon-emitter temperature. Since the occupation numbers for 29 cm^{-1} phonons in ruby are always much less than unity if a pulsed thermal source is used, so that the probability of the phonon-phonon interaction is low, the motion of

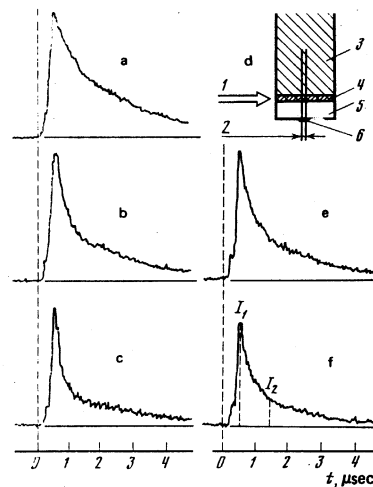


FIG. 1. Form of phonon-detector signal at various concentrations C of the excited chromium ions (cm^{-3}) and at the following amplitudes U of the pulse on the heater (volts: a) $1.0 \cdot 10^{16}\text{ cm}^{-3}$, 40 V; b) $3.4 \cdot 10^{15}\text{ cm}^{-3}$, 40 V; c) $5.0 \cdot 10^{14}\text{ cm}^{-3}$, 40 V; e) $1.0 \cdot 10^{16}\text{ cm}^{-3}$, 20 V; f) $1.0 \cdot 10^{16}\text{ cm}^{-3}$; 8 V. d) Image of sample on the entrance slit of the mono-chromator: 1—direction of exciting radiation, 2—mono-chromator slit, 3—ruby, 4—excited ruby, 5—leucosapphire, 6—film heater.

the resonant phonons cannot depend on the heater temperature. A temperature dependence of the signal waveform would indicate by the same token that phonons with different frequencies, both resonant and nonresonant, take part in the population of the $2\bar{A}$ state of the phonons.

It was assumed in the experiment that the frequency difference can influence the character of the phonon motion: the nonresonant phonons, whose frequency is higher than that of the resonant ones, are more strongly scattered in the crystal. To make this difference stand out more in the motion, the phonons were detected not near the heater, but 3 mm away from it. As shown by preliminary experiments, the detecting volume in the ruby is surrounded by a halo of excited chromium ions. To eliminate the phonon scattering in the halo, a non-uniformly activated sample was used, with a three-millimeter layer between the detector and the heater, consisting of leucosapphire containing no chromium. Provision was made in the experiment to vary the concentrations of the excited chromium ions in the detector by placing neutral light filters in the excitation channel. The relative change of the concentration was determined by registering the intensity of the luminescence of the ruby at the wavelength of the R_1 line. To obtain the absolute value of the concentration we measured, at one of the points, the intensity of the exciting light (in photons/cm²sec), the absorption coefficient of the ruby at the excitation wavelength, and the lifetime of the 2E level.

Figure 1 shows the waveform of the R_2 luminescence pulses registered under various conditions. As seen from the figure the detected pulse can be represented as a sum of two exponentials, fast and slow, and the change of the waveform of the pulse when the experimental conditions are changed reduces primarily to a change of the ratio of the components. The position of the leading front of the fast component leaves no doubt that it is due to the entry of ballistic transverse phonons into the detecting volume at the instant of time $t=l/v \approx 0.6 \mu\text{sec}$. The slow component can in principle be due both to the phonons diffusing towards the detector and to ballistic phonons retained in the detecting

volume because of multiple scattering by the excited chromium ions (the effect of dragging of the resonant phonons¹). An analysis of the experimental data has shown that the damping time of the slow component remains constant at $1.0 \pm 0.1 \mu\text{sec}$ when the concentration of the excited chromium ions in the detector changes. The absence of a concentration dependence means that the main contribution to the signal detected after the end of the ballistic pulse is made by the phonons diffusing through the unexcited crystal.

The experimental data shown in Figs. 1a, 1e, and 1f point to a substantial dependence of the ratio of the fast and slow components on the power of the thermal pulses. Figure 2 shows the results of a quantitative analysis of this dependence. We measured the signals at two different instants of time: the values I_1 and I_2 corresponded to the maximum of the pulse and to $1.5 \mu\text{sec}$ after the application of the electric pulse to the heater. As shown in Fig. 1, the values I_1 and I_2 characterize respectively the amplitudes of the ballistic and diffusion components.

The experiment was performed at maximum ($C \approx 10^{16} \text{cm}^{-3}$) concentration of the excited chromium ions in the detector. In the analysis of the experimental data, account was taken of the fact that the phonons injected in the crystal have a Planck distribution,⁶ and that the temperature of the phonon radiation is connected with the electric power P and with the voltage U applied to the heater by the relation $T \sim P^{1/4} \sim U^{1/2}$ (the Stefan-Boltzmann law). In this model, the signal I_ν obtained when phonons of a definite frequency ν are registered is connected with the heater voltage by the relation

$$I_\nu(U) \sim \exp(-\nu/k\alpha U^{1/2}),$$

where α is a coefficient that takes the heater characteristics into account and k is Boltzmann's constant. This formula is valid if $\nu > k\alpha U^{1/2}$. It is seen from Fig. 2 that this formula describes with a high degree of accuracy the experimental $I_1(U)$ and $I_2(U)$ dependences. In the scale of the figure, the slopes of the straight lines are proportional to the frequencies of the registered phonons. From the ratio of the slopes it follows that the average frequency of diffusing phonons is 1.25 times larger than that of the ballistic phonons.

The difference between the physical natures of the ballistic and diffusion phonons manifests itself in the difference between the concentration dependences of

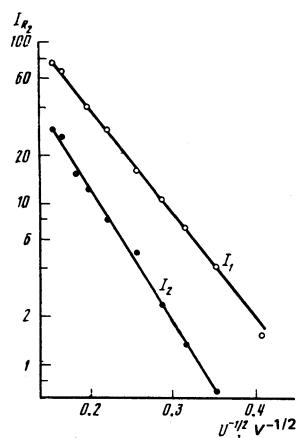


FIG. 2. Plots of the fast (I_1) and slow (I_2) components of the pulse against the heater voltage U ; I_{R_2} is in relative units.

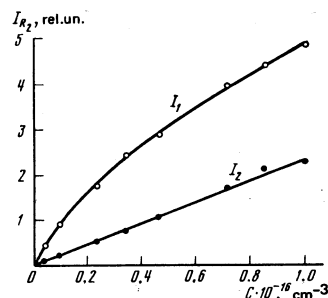


FIG. 3. Plots of the fast (I_1) and slow (I_2) components of the pulse on the concentration C of the excited chromium ions.

I_1 and I_2 (Fig. 3). The concentration dependence of the amplitude of the ballistic pulse (I_1) is clearly sublinear, whereas the diffusion component I_2 increases linearly in the entire range of variation of the concentrations of the excited chromium ions.

The use of a sample with a sapphire layer does not make it possible to interpret the dependence of I_1 on C as the result of absorption in the halo, whose density depends on the concentration. Using the theoretical value of the cross section for the resonant absorption of phonons of frequency 20 cm^{-1} , excited by chromium ions ($\sigma_m = \lambda^2/2\pi \approx 5 \cdot 10^{-14} \text{ cm}^2$), it is easy to verify that the nonlinearity in the concentration dependence of I_1 corresponds to those values of C at which the reciprocal of the resonant-absorption coefficient becomes comparable with the thickness of the excited layer. Inasmuch as in elastic scattering the decrease of the mean free path of the resonant phonons, to a value lower than the dimension of the excited volume, can by itself not lead to nonlinearity of the concentration dependence of the signal, the amplitude nonlinearity and the short duration of the pulse mean that the registered phonons leave the excited volume as a result of one or several scattering acts. The reason may be the change in the mode composition of the phonon radiation as a result of the scattering, a change that leads to production of phonons of weakly absorbed modes,³ to diffuse reflection of the ballistic beam from the boundary of the resonantly scattering medium, or to inelastic scattering by the excited chromium ions.

Assuming 29 cm^{-1} to be the frequency of the ballistic phonons and using the previously considered results of measurements at various source temperatures, we can conclude that the frequencies of the diffusion phonons are grouped around 36 cm^{-1} . The linear character of the concentration dependence of the amplitude of the slow component I_2 points to a small absorption cross section of such phonons by excited chromium ions. A difference by a factor 10^3 – 10^4 between the frequencies of the ballistic and diffusion phonons does not exceed the width of the $\bar{E} - 2\bar{A}$ transition ($\Delta E = 0.012 \text{ cm}^{-1}$, Ref. 4), so that the slow component cannot be attributed to phonons absorbed on the short-wave wings of the resonant line.

It can be concluded on the basis of the results that in experiments on fluorescent detection of the thermal pulses in ruby one can register not only the resonant phonons, but also phonons whose frequency exceeds substantially the frequency of the $\bar{E} - 2\bar{A}$ transition. The steep frequency dependence of the phonon elastic-scattering cross section in the unexcited crystal causes the nonresonant phonons, unlike the ballistic resonant ones, to move diffusely.

One can visualize two schemes of population of the $2\bar{A}$ state with participation of high-frequency phonons: either by nonresonant (Raman) absorption with simultaneous production of a phonon having the difference frequency, or by decay of the high-frequency phonon, as it moves from the heater to the detector, into two phonons, one of which has a frequency 29 cm^{-1} and can be resonantly absorbed. To explain the linear concen-

tration dependence of the amplitude of the diffusion component within the framework of the second scheme it must be assumed that the decay results in formation of only weakly absorbed resonant phonons (longitudinal phonons propagating along the C_3 axis³). Since the diffusing phonons move in all directions and can decay into both longitudinal and transverse phonons, for there are no grounds whatever for this assumption, and preference must be given to the Raman process in the interpretation of the mechanism that populates the $2\bar{A}$ state.

The spectral dependence of the efficiency of the Raman process can be qualitatively represented as a band whose maximum lies on the short-wave side of the resonant frequency (apparently, near 36 cm^{-1}). On the low-frequency side, this band is limited by the decrease of the crystal phonon-state density at the difference frequency, while the high-frequency limit is due to the increase in the rate of anharmonic decay and by the decrease of the phonon mean free path with respect to scattering with increase of frequency. It is obvious that such a spectrum depends on the distance between the heater and the detector and undergoes a certain frequency shift during the time of the luminescence pulse R_2 .

The paradox in the conclusion that the $2\bar{A}$ state is non-resonantly populated is that the theoretically estimated probability of the Raman process is smaller by at least three decades than needed to explain the observed effect. The cause of this discrepancy is apparently the inadequacy of the Debye model used in the theoretical calculations to describe the interaction between the crystal oscillations and the impurity center. In particular, as shown in Ref. 7, the Raman process can be strongly influenced by local oscillations due to the differences of the masses and of the elastic constants of the impurity ion and of the lattice ions. Favoring the presence of such oscillations in ruby is the anomalous shape, observed in Ref. 8, of the phonon wing in the immediate vicinity of the R_1 line. Further clarification of this situation calls for additional experiments that are beyond the scope of the present study.

The authors thank G. I. Romanova for preparing the sample and B. Z. Malkin for a theoretical estimate of the probability of the Raman process.

¹K. F. Renk and J. Deisenhofer, Phys. Rev. Lett. **26** 764 (1971).

²A. P. Abramov, I. N. Abramova, I. Ya. Gerlovin, and I. K. Razumova, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 3 (1978) [JETP Lett. **27**, 1 (1978)].

³S. A. Basun, A. A. Kaplyanskiĭ, and V. L. Shekhtman, *ibid.* **30**, 275 (1979) [**30**, 255 (1979)].

⁴H. Lenfellner, G. Pauli, W. Heisel, and K. F. Renk, Appl. Phys. Lett. **29**, 566 (1976).

⁵S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyi rezonans (Electron Paramagnetic Resonance), Nauka, 1961 [Academic, 1964].

⁶O. Weis, Z. Ang. Phys. **26**, 325 (1969).

⁷M. B. Walker, Phys. Rev. **162**, 199 (1967).

⁸S. E. Stokowski, S. A. Johnson, and P. L. Scott, Phys. Rev. **147**, 544 (1966).