Anisotropy of resonant absorption of high-frequency 0.87×10^{12} Hz phonons in the excited state of Cr^{3+} ions in ruby

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The dependence of the cross section of 0.87×10^{12} Hz phonon absorption, in the transition $\bar{E} \rightarrow 2\bar{A}$ in the excited state of Cr^{3+} ions, on the propagation direction and on the phonon polarization is determined by optical detection of thermal pulses in ruby. The observations agree with the group-theoretical selection rules.

In connection with the appearance of new methods of phonon spectroscopy, a number of investigations have been recently performed of resonant absorption of high-frequency phonons (10^{11}–10^{12} Hz) in transitions between electronic levels of impurity states in crystals.[1–3]

We have observed, for the first time, a dependence of the cross sections for the absorption of 0.87×10^{12} Hz phonons in transitions between the sublevels $\bar{E} \rightarrow 2\bar{A}$ of the excited Cr^{3+} ion in Al_2O_3 crystals on the propagation direction and on the polarization of the phonons. This has made it possible to investigate the question of selection rules for high-frequency phonon transitions, which heretofore has been studied very little experimentally. (In a recent paper[1] on the absorption of 250-GHz phonons in V^{3+} ions in Al_2O_3 it is stated that the theoretical selection rules are strongly violated.)

The investigations were performed by a variant of a new procedure proposed by Renk[2,4], in which the high-frequency phonons propagating in the lattice in the form of thermal pulses are detected optically.[5] The experimental setup is illustrated in Fig. 1. An oriented single crystal Al_2O_3 : 0.05% Cr, measuring $6 \times 6 \times 12$ mm, is placed in liquid helium ($T = 2$ °K). A thin-film constantan heater H is deposited on the face of the sample, and current pulses of duration 20–100 nsec are passed through the heater at a repetition frequency 100 kHz. The Joule heating of the film injects into the crystal phonons with average frequency $\omega \sim 3(kT_H/\hbar)$ (T_H is the heater temperature), and propagates through the crystal in the form of a thermal pulse.[2]

A laser beam passing through the sample ($\lambda = 4400$ Å) excites the Cr^{3+} ions via the $^4A_2$–$^4T_1$ absorption band to

FIG. 1.

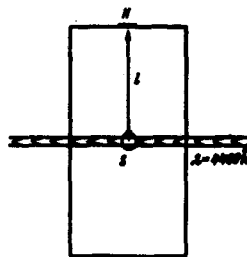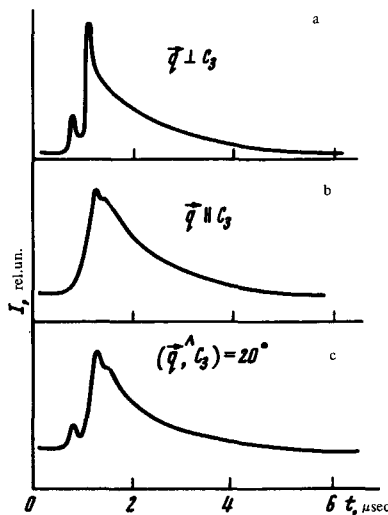FIG. 2.

the doublet $\overline{E} - 2\overline{A}$ ($\Delta = 29$ cm^{-1}) metastable ^2E state, from which $^2E \to {}^4A_2$ luminescence then takes place. With the aid of light pipe S, the radiation from a small volume (~ 0.3 mm^3) located at a distance l from the heater is projected on the slit of a double monochromator tuned to the R_2 line ($2\overline{A} - {}^4A_2$). At 2 °K, only the lower sublevel $\overline{E}$ is populated in practice, and the transition $\overline{E} - {}^4A_2$ (the R_1 line) predominates in the luminescence. When a thermal pulse passes through the detecting volume, the resonant absorption of the 29 cm^{-1} (0.87×10^{12} Hz) phonons gives rise to $\overline{E} \to 2\overline{A}$ transitions, and the R_2 line ($2\overline{A} \to {}^4A_2$) becomes enhanced in the luminescence spectrum. A special photoelectric-registration system at the exit from the monochromator has made it possible to measure the time dependence of the R_2-line intensity, which is given in the case of weak absorption by

$$I(t) \sim n_\omega(t) a N^*, \tag{1}$$

where $n_\omega(t)$ is the number of 0.87×10^{12} Hz phonons in the detecting volume, N^* is a concentration of the excited Cr^{3+} ions, a is the total absorption cross section per Cr^{3+} ion ($a \sim \langle E|H'|2\overline{A}\rangle^2/v^3$, where v is the phonon velocity and $\langle E|H'|2\overline{A}\rangle^2$ is the square of the matrix element of the transition.[6] In view of the low intensity of the R_2 pulse, a counting procedure with accumulation in the multichannel analyzer was used.

The measurements were performed at different phonon propagation directions (q), determined by the position of the line between the heater and the detecting volume in the crystal (see Fig. 2). When the phonons propagate in the basal plane (q$\perp C_3$), two R_2-luminescence pulses are observed (Fig. 2a). Their steep leading fronts correspond to the appearance in the detecting volume of ballistic 0.87×10^{12} Hz, phonons that did not experience scattering in their travel from the heater.[5] The velocities ($v_{ph} = \lambda/t_0$) of the corresponding phonons, calculated from the times t_0 of the appearance of the two pulses, namely $v_1 = 11.4 \times 10^5$ cm/sec and $v_2 = 6.6 \times 10^5$ cm/sec, are close to the known velocities of the longitudinal and "fast" transverse sound propagating in the basal plane in Al$_2$O$_3$. The R_2 pulse from the "slow" transverse sound is apparently superimposed on the preceding pulse and is not resolved in Fig. 2a.

When the phonons propagate along the trigonal axis (q$\|C_3$, Fig. 2b), only one R_2 pulse is observed, with velocity $v = 5.9 \times 10^5$ cm/sec close to the velocity of the transverse sound along C_3. A small inflection on Fig. 2b in the region of the times for the longitudinal phonons ($v \approx 10.2 \times 10^5$ cm/sec) is connected in all probability with the "nonparallelism" of the phonon beam and with the role of the off-axis phonons. This is confirmed by observation of a noticeable enhancement of the "longitudinal" pulse when the direction of q deviates slightly from C_3 (Fig. 2c). The practical absence of a signal from the longitudinal phonons at q $\| C_3$ is not due to the smaller population of the longitudinal modes, which in principle can take place because of singularities in the injection of the thermal pulses and the so-called focusing of the phonons, due to the elastic anisotropy of the crystal.[7] Indeed, measurements of the thermal pulses in pure Al$_2$O$_3$ have shown[7] that at q $\| C_3$ the population of the longitudinal modes is only ~ 1.5 times smaller than the population of the transverse mode, i.e., $n_T \approx 1.5\, n_L$ in (1).

Thus, experiment reveals clearly a strong anisotropy of the cross section of the one-phonon resonance absorption in Cr^{3+}. When the phonons propagate along q$\perp C_3$, the transition $\overline{E} \to 2\overline{A}$ induces longitudinal and transverse 0.87×10^{12} Hz phonons, and when it propagates along C_3 only transverse phonons are induced. The one-phonon transitions are caused by periodic modulation of the crystal field when the lattice is deformed by the sound wave (see, e.g.,[6]). The most general form of the corresponding perturbation operator is $H' \sim \Sigma V_{ij}\epsilon_{ij}$, where ϵ_{ij} and V_{ij} are the strains and the corresponding electron operators, which have the same tensor transformation properties and are symmetrized with respect to the irreducible representations of the point group of the impurity ion.[6]

Let us examine the selection rules for H' in the case of interest to us, that of a transition between the Kramers states $\overline{E}$ and $2\overline{A}$ of the trigonal group C_3 that characterizes the positions of the Cr^{3+} and Al$_2$O$_3$. The direct product is $\overline{E} \times 2\overline{A} = 2E$, where E is the two-dimensional complex-conjugate representation of the group C_3. The deformation pairs $\epsilon_1^\pm = (\epsilon_{zx} \pm i\epsilon_{yz})$ and $\epsilon_2^\pm = (\epsilon_{xx} - \epsilon_{yy} + 2i\epsilon_{xy})$ transform in accordance with E, and are consequently the only ones capable of inducing the transition. In the sound wave we have $\epsilon_{ik} = (u_i q_k + u_k q_i)/2$, where u_i and q_k are the components of the polarization and of the wave vector of the phonon.[6] From this we readily find that in the case of propagation along C_3 ($q_z \neq 0$, $q_x = q_y = 0$), only transverse phonons produce an "active" E deformation that induces a transition. In the case of propagation in the basal plane ($q_z = 0$), the E deformation is produced both by the longitudinal and by the transverse phonons. Thus, the group-theoretical selection rules account adequately for the foregoing experimental facts.

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