ANOMALOUS PARAMAGNETIC RELAXATION OF Nd^{3+} IN YTTRIUM ALUMINUM GARNET

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In the investigation of the physical properties of impurity paramagnetic crystals for use as active media for lasers, an important factor is the study of the EPR spectra and the spin-lattice relaxation (SLR) processes of the lower energy levels of the paramagnetic ions, and also of the mechanisms for energy transfer between them and the other impurity ions.

In the present investigation we studied the EPR spectra and the relaxation processes of Nd^{3+} ions in a laser yttrium aluminum garnet (YAG) crystal $Y_3Al_5O_{12}$. The measurements were performed at a frequency 9.34 GHz in the region of liquid-helium temperatures. The samples were grown in a molybdenum container by the Bridgman horizontal method in a controlled nitrogen atmsophere at a rate of 4 mm/hr. The concentration of the Nd^{3+} ions in the samples was measured by an x-ray luminescence method (see the table).

Measurement of the Nd^{3+} concentration and of the time τ_2 at 4.2°K for different samples

No.	Nd^{3+} concentration in charge, at.%	Nd^{3+} concentration measured, at.%	τ_2 at 4.2°K msec
1	0.18	-	36
2	0.5	0.41	136
3	1.5	0.61	580
4	3.0	2.5	225

The Nd^{3+} ions isomorphically replacing the Y^{3+} ions from six magnetically nonequivalent complexes of orthorhombic symmetry. We determined the principal values of the g-tensor:

$$g_1 = 1.739 \pm 0.002, \quad g_2 = 1.158 \pm 0.001, \quad g_3 = g_2 = 3.908 \pm 0.002,$$

which agrees well with the data of [1].

The relaxation was investigated in greatest detail with the EPR line corresponding to the g-tensor component g_2 and observed in a field H = 3875 Oe. The measurements were performed with a superheterodyne radiospectrometer by a pulsed saturation method, particular attention being paid to the linearity of the apparatus [2].

The observed relaxation curves were of the double-exponential type. The relative weights of the fast exponential decreased with decreasing temperature and depended on the duration of the saturating pulse, increasing with decreasing length of the latter. The char-

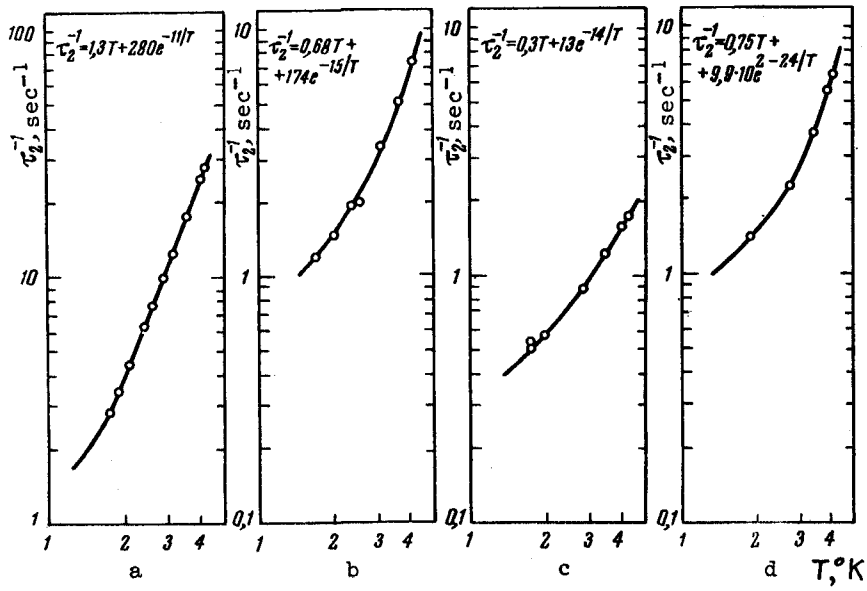

Fig. 1. Temperature dependences of the relaxation rates τ_2^{-1} for YAG samples with different Nd^{3+} concentrations: a - 0.18%, b - 0.41%, c - 0.61%, d - 2.5%.

acteristic times τ_1 and τ_2 of the fast and slow exponentials turned out to depend strongly on the temperature and on the Nd^{3+} concentration. Figure 1 shows the temperature dependences of τ_2^{-1}, and the table lists the values of τ_2 at 4.2°K for samples with different Nd^{3+} concentrations.

The presented data offer evidence of the anomalous character of the relaxation of Nd^{3+} in the YAG. The presence of two exponentials and the dependence of the form of the relaxation curves on the duration of the saturation indicate the presence of cross relaxation [3], but the observed strong dependence of τ_1 on the temperature shows that we are apparently dealing here with unusual cross relaxation processes. Attention is called also to the anomalous concentration dependence of τ_2. The Kronig - Van Vleck theory predicts independence of the SLR on the concentration, but an increase is observed with increasing conenctration for ions of the iron group and of rare earths (see, e.g., [4,5]). We observed an opposite dependence, namely a decrease of the relaxation rates with increasing Nd^{3+} concentration.

Having analyzed the possible causes of the indicated anomalies, we believe that they are connected with effects of cross relaxation between the Nd^{3+} levels and the excited levels of extraneous impurity ions, the concentration of which we assume to be approximately the same in all the investigated samples [1].

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[1] The presence of such impurities is perfectly probable, since no special measures were taken to purify the initial charge or to prevent diffusion of the impurities from the container material during the growth process. In view of the abundance of hfs lines from the isotopes Nd^{143} and Nd^{145} in each of the six complexes, and in view of the low content of the indicated impurities, we have been unable to separate their EPR spectra, but it can be assumed that their concentration is $\lesssim 10^{-2}$ at.%.

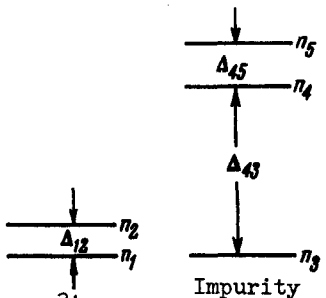

Fig. 2. Level scheme of Nd^{3+} and of the extraneous impurity ion.

Following [3], we can write down the kinetic equations for the populations n_i of the Nd^{3+} level system and of the excited doublet of the impurity (Fig. 2), which we assume to be a Kramers doublet, in the form:

$$\dot{x} = -T_{1x}^{-1}(x - x_0) + w'(y - \beta x),$$
$$\dot{y} = -T_{1y}^{-1}(y - y_0) - \frac{w'}{m}(y - \beta x). \qquad (1)$$

Here $x = n_1 - n_2$, $y = n_4 - n_5$, x_0 and y_0 - equilibrium values of the population differences, $\beta = y_0/x_0$, T_{1x} and T_{1y} - SLR times of Nd^{3+} and of the excited doublet of the impurity ion, and $w' = wn_2^m$, where w and m - probability and multiplicity of the cross-relaxation transitions between their levels. Solution of (1) yields

$$x = A\exp(-t/r_1) + B\exp(-t/r_2) + x_0, \qquad (2)$$

where, assuming $(T_{1y}^{-1} - T_{1x}^{-1}) \ll w'\beta$, we get

$$r_1^{-1} \simeq T_{1y}^{-1}(1 - a) + T_{12}^{-1} + aT_{1x}^{-1},$$
$$r_2^{-1} \simeq T_{1x}^{-1}(1 - a) + aT_{1y}^{-1}, \qquad (3)$$
$$a = \frac{m\beta}{1 + m\beta}, \quad T_{12}^{-1} = \frac{w'}{m}(1 + m\beta),$$

and A and B are constants determined by the initial condition; in particular, when the transition $1 \leftrightarrow 2$ is saturated by short and long pulses of duration τ, we have:

$$B/(A+B) = (r_1^{-1} - r_2^{-1})^{-1}(\beta w' + T_{1x}^{-1} - r_1^{-1}), \ (\tau \ll T_{12}), \qquad (4)$$

$$B/(A+B) = (r_1^{-1} - r_2^{-1})^{-1}\left(\frac{w'\beta T_{1y}^{-1}}{T_{1y}^{-1} + w'/m} + T_{1x}^{-1} - r_1^{-1}\right), \ (\tau \gg T_{12}) \ . \qquad (5)$$

If C_{Nd} and C_{imp} are the concentrations of the Nd^{3+} ions and the impurity, then, assuming $\Delta_{43} \gg kT \gg \Delta_{45}$, we have

$$\Delta_{12}\beta \simeq \frac{C_{imp}}{C_{Nd}} m\exp(-\Delta_{43}/kT)$$

and from (3) we get for the relaxation rates

$$r_1^{-1} \simeq \frac{w'}{m} + T_{1y}^{-1}, \quad r_2^{-1} \simeq T_{1x}^{-1} + \frac{C_{imp}}{C_{Nd}} m^2 T_{1y}^{-1}\exp(-\Delta_{43}/kT). \qquad (6)$$

If we make an assumption that is reasonable in the case of a Kramers system, namely that the relaxation of the excited doublet proceeds via a lower level, then T_{1y} depends little on the temperature [2,3]. Then formulas (2) - (6) provide a qualitative explanation of the presented experimental data for the temperature and concentration dependence of the rate of the slow exponential, and also the dependence of its relative weight on the temperature and

duration of the saturating pulses. The scatter of the parameters of the empirical $\tau_2^{-1}(T)$ curves is apparently connected with the narrowness of the temperature-measurement interval, where the simultaneous presence of linearly and exponentially varying terms admits of a certain indeterminacy in the determination of these parameters. It should be noted that the exponential term in $\tau_2^{-1}(T)$ is not connected with relaxation via the excited Nd^{3+} level, since the latter is separated from the fundamental one by $\Delta = 134$ cm^{-1} (= 193°K) [6]. As to the observed strong temperature dependence of the relaxation rate τ_1^{-1} for the fast exponential, it can be explained according to (6) by assuming a cross-relaxation mechanism in which phonons take part, such as considered in [7].

We are planning experiments with specially pure crystals and in a broader temperature interval for a direct confirmation of the mechanism proposed here for the relaxation of Nd^{3+} via impurities.

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LUMINESCENCE INDUCED IN GALLIUM PHOSPHIDE BY INFRARED LIGHT

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In 1963, Gross and Nedzvedskii [1] noted that infrared radiation increases the photoluminescence of gallium-phosphide samples at low temperatures. Our investigations of this phenomenon have shown that this effect is very appreciable under certain conditions, and have also made it possible, in our opinion, to explain the physical mechanism of this phenomenon.

Figure 1 shows an oscillogram of the signal from an FEU-36 photomultiplier used to register the recombination radiation of a sample of gallium phosphide (n-type, $N_d - N_a = 10^{17}$ cm^{-3}) [1], kept, for example, at the temperature of pumped-off liquid nitrogen. At the in-

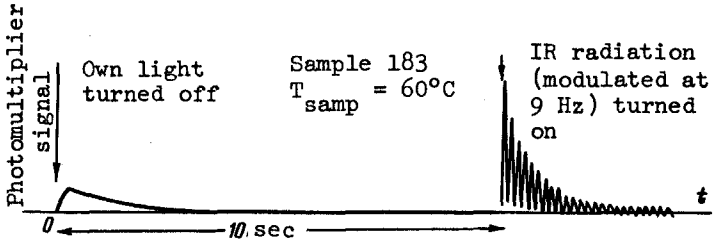

Fig. 1

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