THE EFFECT OF CROSS RELAXATION ON POPULATION INVERSION IN RUBY

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Results are presented of an investigation of the inversion of spin-level populations induced by a pumping signal in ruby (Al_2O_3 with an admixture of Cr^{3+} ions) for various angles θ between the crystal symmetry axis and the direction of the external magnetic field. Indication was performed at a frequency of 3000 Mc/sec; the pumping signal varied between 9 and 17 Gc/sec. The observations were carried out at 4.2 and 1.8°K. Crystals with Cr^{3+} concentrations of 0.001, 0.01, 0.02, 0.35, and 0.12% were studied. The extrema found in the angular dependence of inversion are explained by cross relaxation effects. It is pointed out that it should be possible to design a paramagnetic amplifier having a signal frequency higher than the pumping frequency by using substances with two paramagnetic admixtures.

1. INTRODUCTION

SEVERAL recent papers are devoted to the study of cross relaxation [1] in paramagnetic substances (see, for example, [1-9]). The interest in this phenomenon is to a large extent explained by the great effect it has on the basic parameters of a three-level paramagnetic amplifier.

In the present work the effect of cross relaxation on the inversion of the spin-level populations has been investigated in monocrystalline ruby with the following nominal concentrations of Cr^{3+} ions: 0.001, 0.01, 0.02, 0.035, and 0.12%. The experiments were performed at 4.2 and 1.8°K. In the course of the experiments a change in the resonant paramagnetic absorption χ''_{max} corresponding to transitions between energy levels 3 and 4 (the levels are numbered in order of increasing energy) was observed during the application of auxiliary radiation (the "pump") of sufficient intensity to cause practically complete saturation of the 2—4 or 1—4 transition. The change in the populations of the levels under influence of the pumping signal was estimated by using the inversion coefficient I, defined as the ratio of the quantity χ''_{max} with the pump on to χ''^{0}_{max} with the pump off. The measurements of I were carried out at different values of the angle θ between the direction of the constant magnetic field H_0 and the crystal symmetry axis, while the frequency ν_{34} ($h\nu_{ij} = E_i - E_j$, $i, j = 1, 2, 3, 4$) was kept constant and equal to 3000 Mc/sec by a corresponding change in the field H_0. At the same time the pumping frequency $\nu_p = \nu_{41}$ or $\nu_p = \nu_{42}$ was changed (ν_p was varied in the interval 9—13 or 13—17 Gc/sec, while $\theta = 20-90°$ and $H_0 = 500-1000$ Oe).

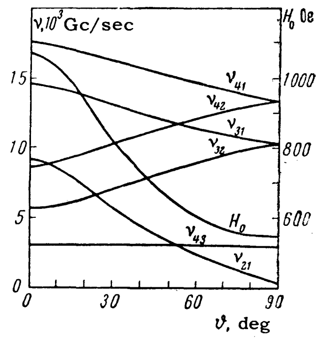

FIG. 1. Angular dependence of H_0 and ν_{ij} for ruby ($\nu_{43} = 3000$ Mc/sec).

The condition ν_{34} = const at once determines the functions $H_0(\theta)$ and $\nu_{ij}(\theta)$, and for specific values of θ the conditions for maximum probability for cross-relaxation transitions are fulfilled: $m\nu_{ij} = n\nu_{kl}$. Figure 1 shows the functions $H_0(\theta)$ and $\nu_{ij}(\theta)$ for ruby given by the condition $\nu_{43} = 3000$ Mc/sec. The graphs were constructed on the basis of tables calculated from the spin Hamiltonian for ruby in the Radio and Electronics Institue of the U.S.S.R. Academy of Sciences. The goals of the experiment were to measure the angular dependence of I and to look for extrema in this dependence that could be associated with cross relaxations.

2. EXPERIMENTAL ARRANGEMENT

In the experimental arrangement the usual bridge-type spectrometer using a superheterodyne receiver with cascade amplification in a TWT was employed. The ruby single crystal was placed

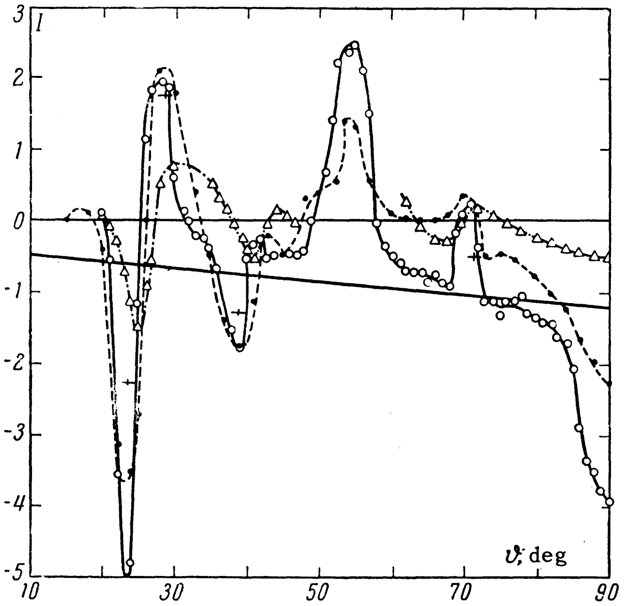

FIG. 2. Angular dependence of the coefficient of inversion of the populations of levels 3 and 4 (during saturation of the transition 2–4) for various Cr^{3+} ion concentrations in Al_2O_3. Δ – concentration 0.035%; ● – 0.020%; ○ – 0.010%; + – data calculated with cross relaxation; heavy line – without cross relaxation. Temperature 1.8° K; ν_{34} = const. = 3000 Mc/sec.

in a resonator tuned to 3000 Mc/sec. The resonator consisted of a quarter-wave strip soldered in a section of shorted waveguide which itself served as a resonator for the pumping signal. In order to maintain a linear relation between χ'' and the observed signal, a small filling factor (0.2) was chosen, and the coupling between the cavity and the external circuit was adjusted to be greater than critical. In view of the large spin-lattice relaxation times in ruby at low temperatures (transitional processes as long as 10 sec have been observed) the measurements were made without magnetic field modulation.

The power of the 3000 Mc/sec generator was kept at a level of 10^{-9} W; the power P of the pump was adjusted for practically complete saturation of the 2–4 (or 1–4) transition (the criterion for saturation was no change in the observed value of I upon a decrease in P of 10–20 dB).

3. EXPERIMENTAL RESULTS

In Fig. 2 are presented the results of measurements of the coefficient of inversion of the populations of levels 3 and 4 during saturation of the 2–4 transition for ruby samples containing nominal atomic concentrations of Cr^{3+} equal to 0.01, 0.02, and 0.035%; the temperature was equal to 1.8°K. In Fig. 2 negative values for I correspond to "paramagnetic emission," the population of level 4 being greater than that of level 3. Characteristically, near $\theta \approx 30°$ saturation of the 2–4 transition increases (I > 1) the difference in the populations of levels 3 and 4; this phenomenon is explained by cross-relaxation transitions associated with the equality $\nu_{21} \approx 2\nu_{43}$ (see below).

Similar measurements were made also at Cr^{3+} concentrations of 0.001 and 0.12%. At the 0.001% concentration the characteristic extrema in $I(\theta)$ were also observed. This indicates that even at this low concentration of paramagnetic ions the probability for cross relaxation is comparable to spin-lattice relaxation probabilities (at $T \sim 4°K$). The decrease in $|I|$ with increasing concentration above 0.01% is explained, apparently, by the increase in the probabilities of cross-relaxation processes of higher orders, which in the limit should lead to equilibrium populations in all the levels, $I_{ij} = 0$. Actually, at a concentration of 0.12% the inversion coefficient was close to zero, and remained within limits of ±0.1 as θ was changed from 20 to 90°.

When the 1–4 transition was saturated, extrema in $I(\theta)$ were again observed, and the character of these extrema confirms their explanation on the basis of cross-relaxation effects (see below). For example, at $\theta \approx 39°$ there is a maximum in I when the 1–4 transition is saturated, in distinction to the case of saturation of the 2–4 transition (at $\theta = 39°$ we have $\nu_{41} \approx 2\nu_{32}$). At 4.2°K the character of the dependence $I(\theta)$ differs little from the results obtained at 1.8°K.

4. DISCUSSION

The majority of the extrema in $I(\theta)$ (Fig. 2) can be explained by the effect of cross-relaxation transitions; for example, the extrema at angles θ equal approximately to 23, 28, 39, and 71° agree well with the values of θ taken from the graphs in Fig. 1, at which we have, respectively $\nu_{32} = \nu_{21}$, $2\nu_{43} = \nu_{21}$, $2\nu_{32} = \nu_{41}$, and $\nu_{43} = 2\nu_{21}$.[1)] To verify this correspondence, similar measurements (at the 0.01% concentration) were made at frequencies ν_{43} equal to 2800 and 3200 Mc/sec. The experimental and calculated values of θ presented in the table confirm this correspondence; additional confirmation exists in the character of the extremum at $\theta = 39°$ when the 1–4 transition is saturated, which was mentioned above.

The effect of cross relaxation on the magnitude of I can be qualitatively explained as a "by-pass-

[1)] The maximum in $I(\theta)$ at $\theta \sim 55°$ is explained by the equality $\nu_p = \nu_{42} = \nu_{31}$.

ν_{43}, Mc/sec	$\nu_{32}=\nu_{21}$		$2\nu_{43}=\nu_{21}$		$2\nu_{32}=\nu_{41}$		$\nu_{43}=2\nu_{21}$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
2 800	20	19.9	30	29.1	34	34.2	71	71.5
3 000	23.5	23.5	28.5	29.0	39	38.4	71	71.5
3 200	27	26.9	28	28.9	42	42.3	71.5	71.5

ing" of the signal or idler transitions: cross relaxation between any transitions improves the thermal contact of these transitions with the lattice, and the well-known expression for the inversion coefficient in the case of three levels [10]

$$I = 1 - \nu_p/\nu_s\,(1+z), \quad z = w_s/w_i \tag{1}$$

(ν_p is the pump frequency, ν_s the signal frequency, w_s and w_i are the spin-lattice relaxation probabilities for the signal and idler transitions, respectively) shows that with increasing w_s the inversion coefficient I increases, but with increasing w_i, it decreases. In the case of four levels I can be represented by a form similar to Eq. (1), but the parameter z now equals

$$z = (w_s + w_{13}w_{14}/w_1)/(w_i + w_{13}w_{12}/w_1), \qquad w_1 = \sum_{i=2}^{4} w_{ij}, \tag{2}$$

and the conclusions regarding the effect of shunting the signal or idler transitions still hold good. In this it has been assumed that the pump acts between levels 2 and 4 and the signal transition is 3—4, $w_s \equiv w_{34}$, and $w_i \equiv w_{23}$.

The shunting mechanism can be visualized as follows. If there are in the paramagnet any two transitions connected by the relation $m\nu_{21} = n\nu_{ba}$, and the probability of a cross-relaxation transition by which m transitions $2 \to 1$ and n transitions $a \to b$ simultaneously occur is much larger than the probability of a spin-lattice relaxation, then it is easily shown [7] that

$$T_{21} = T_{ba}, \tag{3}$$

where T_{ij} is the "spin" temperature defined by the relation $N_i/N_j = \exp(h\nu_{ji}/kT_{ij})$. Thus the presence of a shunting transition having a sufficiently large probability for spin-lattice relaxation assists the shunted transition to acquire the lattice temperature. In accordance with this, it can be seen in Fig. 2 that for $\nu_i \equiv \nu_{32} = \nu_{21}$ ($\theta \approx 23°$) and for $\nu_i = \nu_{41}/2$ ($\theta \approx 39°$), the magnitude of I decreases, whereas for $\nu_s = \nu_{21}/2$ ($\theta \approx 29°$) and $\nu_s = 2\nu_{21}$ ($\theta \approx 71°$) I increases.

If the probability for cross relaxation is much greater than w_{ij}, then the coefficient of inversion I can be also represented by Eq. (1). We present below expressions for the parameter z, obtained under the condition $|h\nu_{ji}/kT_{ij}| < 1$, for three special cases ($\alpha = m/n$):

a) for $m\nu_s = n\nu_{21}$ ($\theta \approx 29°$, m = 2, n = 1; $\theta \approx 71°$, m = 1, n = 2)

$$z_a = \frac{w_s + \alpha^2 w_1 - \alpha(w_{13} - w_{14})}{w_i + w_1 - \alpha(w_{13} + w_{14})}; \tag{4a}$$

b) for $m\nu_i = n\nu_{21}$ ($\theta \approx 23°$, m = n = 1)

$$z_b = \frac{w_s - \alpha w_{14}}{w_i + \alpha w_{14} + (1+2\alpha)w_{13} + \alpha^2 w_1}; \tag{4b}$$

c) for $m\nu_i = n\nu_{41}$ ($\theta \approx 39°$, m= 2, n = 1)

$$z_c = \frac{w_s + w_{13} + \alpha(w_{12} + w_{13})}{w_i + \alpha^2 w_1 - \alpha(w_{12} - w_{13})}. \tag{4c}$$

For a rough estimate of the magnitude of I we can take all the w_{ij} to be equal. Then

$$z = 1, \qquad z_a = \frac{1+3\alpha^2}{2-2\alpha}; \qquad z_b = \frac{1+\alpha}{2+3\alpha+3\alpha^2}; \qquad z_c = \frac{2}{1+3\alpha^2}. \tag{5}$$

In Fig. 2 the continuous straight line corresponds to the case z = 1 (absence of cross relaxation), whereas the points shown as crosses are calculated from Eq. (5). It can be seen from Fig. 2 that the behavior of $I(\theta)$ agrees rather well with the results of calculation from Eqs. (1), (2), and (4), even with the very crude assumptions that w_{ij} = const and that at each value of θ only one kind of cross-relaxation transition is effective.

5. THE CASE OF TWO PARAMAGNETIC ADMIXTURES

Cross-relaxation shunting can also take place by means of transitions between the energy levels of another paramagnetic impurity (in Pershan's terminology [8] "impurity-doping" in distinction to the case just considered, "self-doping"). Let us consider the simplest case, where there are two systems of paramagnetic particles—one with three energy levels 1, 2, 3, the other with two levels a, b. Let the transition 1—3 be saturated by the pumping signal and the condition $m\nu_{32} = n\nu_{ba}$ be satisfied; the number of cross-relaxation transitions of the type $m(3 \rightarrow 2)$, $n(a \rightarrow b)$ per unit time will be equal to $wN_3^m N_a^n$. Then under the condition $|h\nu_{ji}/kT_{ij}| \ll 1$, the change in the population of level 2 as a consequence of cross relaxation will equal (per unit time)

$$dN_2/dt = mA\left[\tfrac{1}{2}mN'(N_3 - N_2) - \tfrac{1}{3}nN(N_c - N_a)\right], \quad (6)$$

where $A \equiv w(N/3)^{m-1}(N'/2)^{n-1}$, and N and N' are the number densities of the particles with three and two levels, respectively.

From this can be obtained the following expression for the inversion coefficient of the 2—3 transition:

$$I_{23} = 1 - \frac{\nu_{31}}{\nu_{32}(1+z)},$$

$$z = \frac{1}{w_s}\left[w_i + \frac{Am^2N'/2}{An^2N/3 + w_{ab}} w_{ab}\right]. \quad (7)$$

Under the condition that the cross-relaxation probability be much greater than w_{ab}, i.e.,

$$An^2N/3w_{ab} \gg 1, \quad (8)$$

the term shunting w_s in Eq. (7) becomes equal to $\alpha^2 w_{ab}(N'/2)(N/3)^{-1}$. A similar result is also obtained in the case of shunting of the idler transition 1—2.

According to Pershan[8] the presence of an impurity with levels a, b such that $m\nu_{32} \equiv n\nu_{ba}$ increases the inversion coefficient I_{23}, i.e., it diminishes the number of active particles in the 2—3 transition. The problem can be considered in reverse-obtaining amplification at frequency ν_{ba} by saturating the transition 1—3. It is not difficult to show that the inversion coefficient for the transition a—b equals

$$I_{ab} = \left[1 + \frac{An^2N}{3w_{ab}} I_{23}\right] \Big/ \left[1 + \frac{An^2N}{3w_{ab}}\right] \quad (9)$$

and when condition (8) holds

$$I_{ab} = I_{23}. \quad (10)$$

This very same result also follows directly from Eq. (3). Thus, a crystal with two paramagnetic impurities can be used as a paramagnetic amplifier at a signal frequency exceeding the pump frequency ($\nu_{ba} > \nu_{31}$), in particular, as an amplifier of millimeter waves; since the concentration N' is larger than in the usual amplifying crystals and the signal frequency ν_{ba} is large, it will be possible to obtain a large number of active particles $N_b - N_a$ (according to Eq. (10), $N_b - N_a = (3N'\nu_{ba}/2N\nu_{32})(N_3 - N_2)$).

CONCLUSION

In the case of substances having relaxation times of the order of 0.1 sec (ruby at liquid helium temperatures) at paramagnetic ion concentrations $> 10^{-4}$, cross relaxation determines to a significant extent the inversion attainable in the three-level method. An estimate of the inversion coefficient assuming w_{ij} = const agrees qualitatively with experiment. In the case of substances containing two impurities cross relaxation can be used to realize a paramagnetic amplifier whose signal frequency is greater than its pump frequency.

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