Fisher and McSkimin[21] have pointed out the existence of some sort of higher order phase transition in uranium at 42°±1°K, based on anomalies noted in the thermal expansion, Hall coefficient, electrical resistivity, and thermoelectric power. Furthermore, the transition apparently is characterized by both an inflection point in the entropy vs temperature curve and by a vanishing thermal expansion coefficient.[22] It is thus not clear what the course of the transition at higher pressures might be and, in fact, it may be that measurements of dT/dP might be a fruitful approach in determining the order of this transition.

[21] E. S. Fisher and H. J. McSkimin, Phys. Rev. **124**, 67 (1961).
[22] C. S. Barrett, M. H. Mueller, and R. L. Hitterman, Phys. Rev. **129**, 625 (1963).

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Gary Higgins for having supplied us samples of uranium without which this investigation would not have been possible. Our thanks are due to R. C. Newton for much encouragement, to Dr. W. F. Libby for having critically read the manuscript, and to T. J. Thomas who kept our apparatus in good repair.

PHYSICAL REVIEW VOLUME 129, NUMBER 5 1 MARCH 1963

Nuclear Spin-Lattice Relaxation in Noncubic or Imperfect Cubic Crystals for $I=7/2$ or $9/2$

D. P. Tewari and G. S. Verma*
Department of Physics, University of Allahabad, Allahabad, India
(Received 22 October 1962)

Detailed calculations of the relaxational behavior of the central resonance line corresponding to transitions between levels $m=\pm\frac{1}{2}$ have been made for $I=\frac{7}{2}$ and $I=\frac{9}{2}$ in noncubic or imperfect cubic crystals. The behavior of the central line depends on the relative values of W_1/W_2 and differs considerably in the two special cases which have been considered.

Recently, the relaxation behavior of the central line corresponding to transitions between levels $m=\pm\frac{1}{2}$ for $I=\frac{3}{2}$ and $\frac{5}{2}$ has been studied by Andrew and Tunstall[1] in imperfect cubic crystals and in noncubic crystals. The two special cases which they have considered are (1) when a strong saturating radio-frequency field is applied to the nuclear spin system which is in equilibrium with the lattice in the presence of an external magnetic field, and (2) when the external field is suddenly applied to the system which is in equilibrium in zero magnetic field. In the present paper we have examined the similar situation for $I=\frac{7}{2}$ and $\frac{9}{2}$.

QUADRUPOLAR RELAXATION FOR $I=7/2$

Figure 1 shows the quadrupolar nuclear transitions for the case $I=\frac{7}{2}$. The differential equations governing the difference in populations of the levels for $I=\frac{7}{2}$ are given by

$$\dot{N}_3=-\frac{1}{3}(6W_1+W_2)N_3+\frac{8}{21}(2W_1+W_2)N_2+\frac{5}{7}W_2N_1-\frac{2}{21}(8W_2-13W_1)n_0,$$

$$\dot{N}_2=\frac{1}{3}(3W_1-W_2)N_3-\frac{2}{21}(16W_1+11W_2)N_2+\frac{5}{21}(W_1+W_2)N_1+\frac{20}{21}W_2N_0+\frac{2}{21}(3W_1+2W_2)n_0,$$

$$\dot{N}_1=\frac{1}{3}W_2N_3+\frac{8}{21}(2W_1-W_2)N_2-\frac{5}{21}(2W_1+7W_2)N_1+\frac{20}{21}W_2N_{-1}-\frac{2}{21}(3W_1-8W_2)n_0, \tag{1}$$

$$\dot{N}_0=\frac{5}{7}W_2N_2+\frac{5}{7}(W_1-W_2)N_1-\frac{40}{21}W_2N_0+\frac{5}{7}(W_1-W_2)N_{-1}+\frac{5}{7}W_2N_{-2}-\frac{10}{21}(W_1-2W_2)n_0,$$

where $N_{m+\frac{1}{2}}=N_{m+1}-N_m$ ($m=\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \pm\frac{7}{2}$) and $n_0=N_{m+1}-N_m$ when no radio-frequency field is applied.

Writing $N_p'=N_p-n_0$, $N_{-1}=N_1$, $N_{-2}=N_2$, and $N_{-3}=N_3$, we obtain the following four equations:

$$\dot{N}_3'=-\frac{1}{3}(6W_1+W_2)N_3'+\frac{8}{21}(2W_1+W_2)N_2'+\frac{5}{7}W_2N_1',$$

* Present address: Millis Science Center, Western Reserve University, Cleveland, Ohio.
[1] E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. (London) **78**, 1 (1961).

$$\dot{N}_2' = \frac{1}{3}(3W_1 - W_2)N_3' - \frac{2}{21}(16W_1 + 11W_2)N_2' + \frac{5}{21}(W_1 + W_2)N_1' + \frac{20}{21}W_2N_0', \quad (2)$$

$$\dot{N}_1' = \frac{1}{3}W_2N_3' + \frac{8}{21}(2W_1 - W_2)N_2' - \frac{5}{21}(2W_1 + 3W_2)N_1',$$

$$\dot{N}_0' = \frac{10}{7}W_2N_2' + \frac{10}{21}(W_1 - W_2)N_1' - \frac{40}{21}W_2N_0'.$$

Assuming the solution to be of the form

$$N_p' = \sum_{q=1,2,3,4} a_{pq}\exp(-\lambda_q t), \quad (3)$$

the four relaxation constants λ_q are given by the four roots of the following quartic equation:

$$\lambda^4 - 4\lambda^3(W_1 + W_2) + \frac{4\lambda^2}{441}(417W_1^2 + 1453W_1W_2 + 435W_2^2) - \frac{40}{21\times21\times7}\lambda(56W_1^3 + 681W_1^2W_2 + 763W_1W_2^2 + 70W_2^3) + \frac{800}{21\times21\times21\times3}(24W_1^3W_2 + 113W_1^2W_2^2 + 63W_1W_2^3) = 0. \quad (4)$$

For the case $W_1 = W_2$, this equation gives four roots $\lambda_1 = 0.476W_1$, $\lambda_2 = 1.333W_1$, $\lambda_3 = 2.381W_1$, and $\lambda_4 = 3.810W_1$. The roots of Eq. (4), for $W_1/W_2 = 0.2$, 0.5, 2.0, and 5.0, have been evaluated and are given in Table I. Variation of the four roots λ/W_1 with W_1/W_2 has also been plotted in Fig. 2.

In case I for which all $N_p' = -n_0$, the growth of the signal for $W_1 = W_2$ is given by

$$N_p/n_0 \equiv 1 - 1.527e^{-0.476W_1t} + 0.903e^{-1.333W_1t} - 0.335e^{-2.381W_1t} - 0.041e^{-3.810W_1t}. \quad (5)$$

The four relaxation times $1/0.476W_1$, $1/1.333W_1$, $1/2.381W_1$, and $1/3.810W_1$ describe the growth of the observed signal. However, initially only the first two exponential terms matter and later on only the first exponential term is significant and the growth is characterized by a single relaxation time $1/0.476W_1$.

In case II, if saturation of the central line is complete N_0' initially is again $-n_0$. For $P \gg W_1$, where P is the transition probability for transitions between $m = \pm\frac{1}{2}$ brought about by the saturating radiation, the other initial values $N_p (p \neq 0)$, for $W_1 = W_2$, are

$N_1' = (29/49)n_0$, $N_2' = -(12/49)n_0$, and $N_3' = (3/49)n_0$.

The growth of the central line is given by

$$N_0/n_0 = 1 - 0.048e^{-0.476W_1t} - 0.818e^{-1.333W_1t} - 0.050e^{-2.381W_1t} - 0.084e^{-3.810W_1t}. \quad (6)$$

Again the return to equilibrium is characterized by four relaxation times but because of the much larger coefficient of the second exponential term, the growth is exponential in nature most of the time with relaxation time equal to $3/4W_1$. For $W_1 = W_2$ the growth of N_0/n_0, to which the nuclear magnetic resonance signal is proportional, has been plotted for both cases in Fig. 3. It may be seen from the figure that there is more rapid growth in case II. The procedure for evaluating the initial values of N_p' is exactly similar to that of Andrew and Tunstall. The values of the coefficients a_{01}, a_{02}, a_{03}, and a_{04} for both cases are given in Table II. Similar calculations have been performed for $W_1/W_2 = 0.2$, 0.5, 2.0, and 5.0. Values of the coefficients are given in Table II and the results of the calculation for the growth of the signal are shown in Figs. 4 to 7. It may be noticed that in all the cases except $W_1/W_2 = 0.2$ the growth in case II is more rapid than in case I. Comparison of the results in the case $W_1/W_2 = 0.2$ with $W_1/W_2 = 0.5$ shows that the growth in case I is more rapid only when W_1 is much less than W_2. For $W_1/W_2 < 0.1$, the coefficients of N_p' for two equations out of the four equations

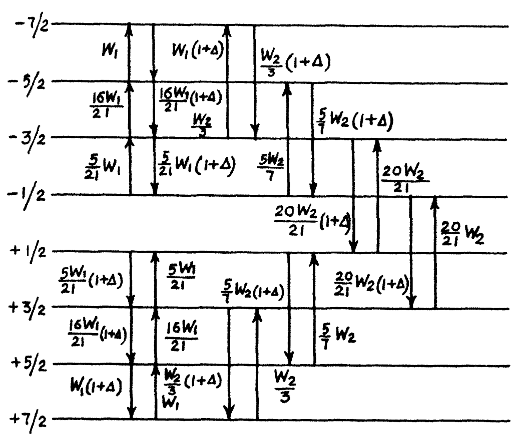

FIG. 1. Transitions effected by the quadrupolar spin-lattice relaxation process for $I = \frac{7}{2}$.

TABLE I. Relaxation constants λ_q for different values of the ratio W_1/W_2, for $I = \frac{7}{2}$.

W_1/W_2	λ_1/W_1	λ_2/W_1	λ_3/W_1	λ_4/W_1
0.2	1.669	2.113	6.386	13.833
0.5	0.836	1.659	3.425	6.081
1.0	0.476	1.333	2.381	3.810
2.0	0.275	0.848	1.996	2.881
5.0	0.123	0.615	1.243	2.820

TABLE II. Relaxation coefficients for different values of the ratio W_1/W_2, for $I=\frac{7}{2}$.

W_1/W_2	Case I a_{01}	Case I a_{02}	Case I a_{03}	Case I a_{04}	Case II a_{01}	Case II a_{02}	Case II a_{03}	Case II a_{04}
0.2	−9.515	9.180	2.378	−1.042	−2.728	2.438	0.445	0.844
0.5	0.831	0.065	0.001	0.103	0.373	−0.250	0.002	0.873
1.0	1.527	−0.903	0.335	0.041	0.048	0.818	0.050	0.084
2.0	1.325	−0.232	−0.063	−0.013	0.309	0.491	0.165	0.036
5.0	0.880	0.260	0.102	−0.242	0.739	0.248	0.004	0.009

of (4) are numerically identical to the third decimal place and hence no attempt has been made to evaluate the four coefficients for such cases.

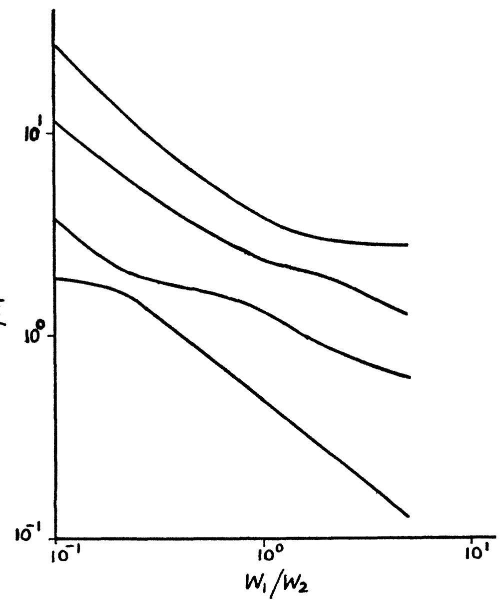

FIG. 2. The four roots λ_q of the quartic equation as a function of W_1/W_2.

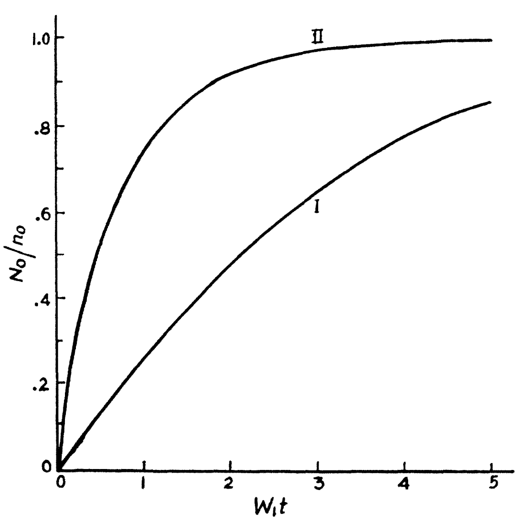

FIG. 3. Growth of N_0/n_0 for $I=\frac{7}{2}$ and $W_1=W_2$.

III. QUADRUPOLAR RELAXATION FOR $I=9/2$

Figure 8 shows the nuclear transitions for the case $I=\frac{9}{2}$. The differential equations governing the difference in populations of the levels are given by

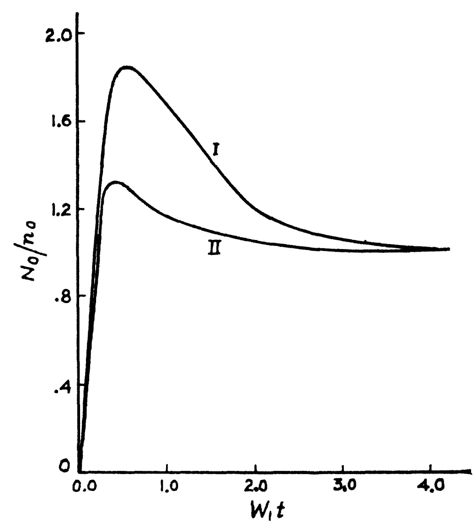

FIG. 4. Growth of N_0/n_0 for $I=\frac{7}{2}$ and $W_1/W_2=0.2$.

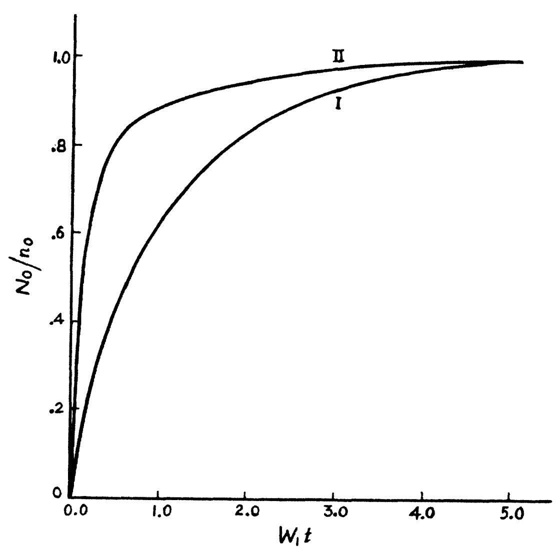

FIG. 5. Growth of N_0/n_0 for $I=\frac{7}{2}$ and $W_1/W_2=0.5$.

$$\dot{N}_4=-\left(2W_1+\frac{W_2}{4}\right)N_4+\left(W_1+\frac{W_2}{3}\right)N_3+\frac{7}{12}W_2N_2+\left(W_1-\frac{2}{3}W_2\right)n_0,$$

$$\dot{N}_3=\left(W_1-\frac{W_2}{4}\right)N_4-\left(2W_1+\frac{5W_2}{6}\right)N_3+\frac{7}{12}\left(W_1+\frac{W_2}{2}\right)N_2+\frac{7}{8}W_2N_1+\frac{n_0}{12}(5W_1-W_2),$$

$$\dot{N}_2=\frac{W_2}{4}N_4+\left(W_1-\frac{W_2}{3}\right)N_3-\frac{7}{24}W_2N_2-\left(\frac{W_1}{6}+\frac{23}{12}W_2\right)N_1-\frac{25}{24}W_2N_0-\frac{5}{6}n_0(W_1-4W_2), \quad (7)$$

$$\dot{N}_1=\frac{7}{12}W_2N_3+\frac{7}{12}\left(W_1-\frac{W_2}{2}\right)N_2-\left(\frac{W_1}{3}+\frac{23}{12}W_2\right)N_1+\frac{25}{24}W_2N_{-1}-\frac{n_0}{4}\left(W_1-\frac{7}{3}W_2\right),$$

$$\dot{N}_0=\frac{7}{8}W_2N_2+\left(\frac{W_1}{6}-\frac{W_2}{6}\right)N_1-\frac{50}{24}W_2N_0+\frac{1}{6}(W_1-W_2)N_{-1}+\frac{7}{8}W_2N_{-2}-\frac{n_0}{3}(W_1-2W_2).$$

Writing $N_{-2}=N_2$, $N_{-1}=N_1$, and $N_p'=N_p-n_0$, the following five equations are obtained:

$$\dot{N}_4'=-\left(2W_1+\frac{W_2}{4}\right)N_4'+\left(W_1+\frac{W_2}{3}\right)N_3'+\frac{7}{12}W_2N_2',$$

$$\dot{N}_3'=\left(W_1-\frac{W_2}{4}\right)N_4'-\left(2W_1+\frac{5W_2}{6}\right)N_3'+\frac{7}{12}\left(W_1+\frac{W_2}{2}\right)N_2'+\frac{7}{8}W_2N_1',$$

$$\dot{N}_2'=\frac{1}{4}W_2N_4'+\left(W_1-\frac{W_2}{3}\right)N_3'-\left(\frac{7}{6}W_1+\frac{35}{24}W_2\right)N_2'+\left(\frac{W_1+W_2}{6}\right)N_1'+\frac{25}{24}W_2N_0', \quad (8)$$

$$\dot{N}_1'=\frac{7}{12}W_2N_3'+\frac{7}{12}\left(W_1-\frac{W_2}{2}\right)N_2'-\left(\frac{W_1}{3}+\frac{7}{8}W_2\right)N_1',$$

$$\dot{N}_0'=\frac{7}{4}W_2N_2'+\frac{1}{3}(W_1-W_2)N_1'-\frac{50}{24}W_2N_0'.$$

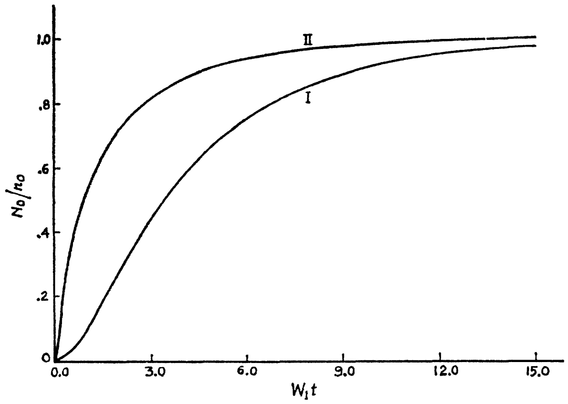

FIG. 6. Growth of N_0/n_0 for $I=\frac{7}{2}$ and $W_1/W_2=2$.

For $W_1=W_2$ the above equations are reduced to

$$\dot{N}_4'=-\frac{9}{4}W_1N_4'+\frac{4}{3}W_1N_3'+\frac{7}{12}W_1N_2',$$

$$\dot{N}_3'=\frac{3}{4}W_1N_4'-\frac{17}{6}W_1N_3'+\frac{7}{8}W_1N_2'+\frac{7}{8}W_1N_1',$$

$$\dot{N}_2'=\frac{W_1}{4}N_4'+\frac{2}{3}W_1N_3'-\frac{63}{24}W_1N_2'+\frac{1}{3}W_1N_1'+\frac{25}{24}W_1N_0', \quad (9)$$

$$\dot{N}_1'=\frac{7}{12}W_1N_3'+\frac{7}{24}W_1N_2'-\frac{29}{24}W_1N_1',$$

$$\dot{N}_0'=\frac{7}{4}W_1N_2'-\frac{50}{24}W_1N_0'.$$

The relaxation constants λ_q are eigenvalues of the

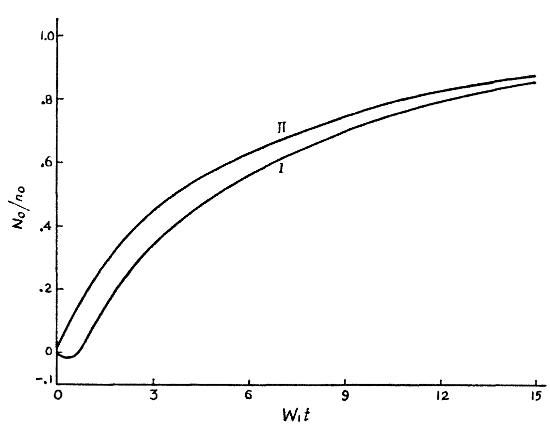

FIG. 7. Growth of N_0/n_0 for $I=\frac{7}{2}$ and $W_1/W_2=5$.

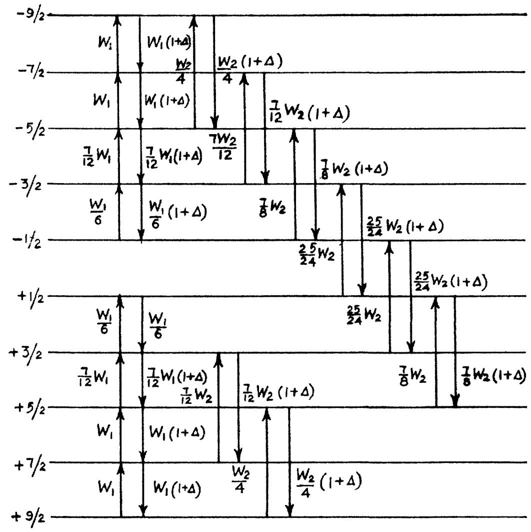

FIG. 8. Transitions effected by the quadrupolar spin-lattice relaxation process for $I=\frac{9}{2}$.

matrix of the coefficients of Eq. (9) and are the roots of the equation

$$\lambda^5-11\lambda^4+\frac{25027}{24\times24}\lambda^3-\frac{1027992}{24\times24\times24}\lambda^2+\frac{8749490}{24\times24\times24\times12}\lambda-\frac{895475}{24\times24\times24\times6}=0. \quad (10)$$

The roots are $\lambda_1/W_1=1/3$, $\lambda_2/W_1=15/12$, $\lambda_3/W_1=43/24$, $\lambda_4/W_1=85/24$, $\lambda_5/W_1=98/24$.

For case I all $N_p'=n_0$ and the values of the coefficients are $a_{01}=1.458$, $a_{02}=0.084$, $a_{03}=-1.090$, $a_{04}=1.000$, $a_{05}=-0.452$. Similarly for case II initially $N_0'=-n_0$, $N_1'=-0.019n_0$, $N_2'=0.097n_0$, $N_3'=-0.295n_0$, and $N_4'=0.624n_0$ and the coefficients are $a_{01}=-0.107$, $a_{02}=-0.063$, $a_{03}=0.902$, $a_{04}=0.000$, $a_{05}=0.268$.

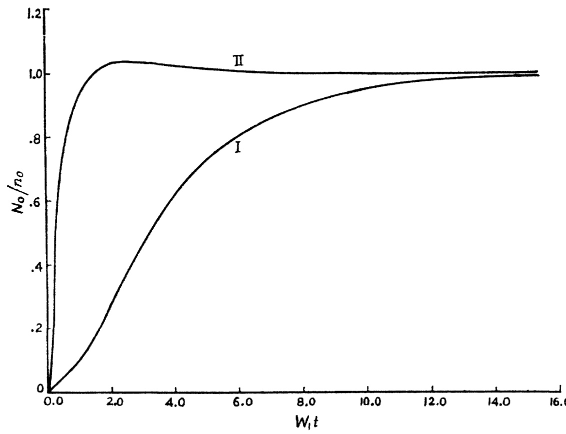

FIG. 9. Growth of N_0/n_0 for $I=\frac{9}{2}$ and $W_1=W_2$.

For case I the growth of the central line is given by

$$N_0/n_0=1-1.458e^{-0.333W_1t}-0.084e^{-1.250W_1t}+1.09e^{-1.792W_1t}-e^{-3.542W_1t}+0.452e^{-4.083W_1t}. \quad (13)$$

The growth in this case is mainly controlled by the first exponential term with relaxation time $1/0.333W_1$. For case II the growth of the central line is given by

$$N_0/n_0=1+0.107e^{-0.333W_1t}+0.063e^{-1.250W_1t}-0.902e^{-1.792W_1t}-0.268e^{-4.083W_1t}. \quad (14)$$

In this case the growth is mainly controlled by the third exponential because of the much larger coefficient. The first and third exponentials also make appreciable contribution to the growth. Thus, in this case, all the four relaxation times matter. The growth of the signal N_0/n_0 for both cases is plotted in Fig. 9. It may again be noticed from this figure that the growth in case II is more rapid.

ACKNOWLEDGMENTS

One of us (D. P. T.) is indebted to University Grants Commission, India for the award of a Research Scholarship.