tation spectra will provide more valuable information on librations and hindered rotations.

We wish to thank Professor W. Känzig and his group for helpful discussions and for growing the crystals.

---

[1] A. J. Khintchin, Math. Ann. 109, 604 (1934).

[2] A. M. Jaglom, Theorie der stationären Zufallsfunktionen (Akademie Verlag, Berlin, Germany, 1959), p. 27.

[3] R. G. Gordon, J. Chem. Phys. 43, 1307 (1965).

[4] C. Brot, J. Phys. (Paris) 28, 789 (1967); B. Lassier and C. Brot, Chem. Phys. Letters 1, 583 (1968).

[5] J. Lascombe, P. V. Huong, and M. L. Josien, Bull. Soc. Chim. France (1959), 1175; M. O. Bulanin and N. D. Orlova, Opt. i Spektroskopiya 4, 569 (1958).

[6] W. Känzig, H. R. Hart, and S. Roberts, Phys. Rev. Letters 13, 543 (1964); K. Knop, G. Pfister, and W. Känzig, Physik Kondensierten Materie 7, 107 (1968).

[7] U. Kuhn and F. Lüty, Solid State Commun. 2, 281 (1964); H. Paus and F. Lüty, Phys. Status Solidi 12, 347 (1965); M. W. Klein et al., Phys. Rev. Letters 17, 521 (1966); M. W. Klein et al., Bull. Am. Phys. Soc. 11, 228 (1966); M. W. Klein et al., Bull. Am. Phys. Soc. 12, 78 (1967); P. Handler and D. E. Aspnes, Phys. Rev. Letters 17, 1095 (1966).

[8] A. S. Devonshire, Proc. Roy. Soc. (London), Ser. A 153, 601 (1936).

[9] P. Sauer, Z. Physik 194, 360 (1966).

[10] F. K. Kneubühl, to be published.

[11] H. Shimizu, J. Chem. Phys. 43, 2453 (1965), and Bull. Chem. Soc. Japan 39, 2385 (1966).

[12] M. Ch. Wang and G. E. Uhlenbeck, Rev. Mod. Phys. 17, 323 (1945).

[13] P. Debye, Polar Molecules (Chemical Catalog Company, Inc., New York, 1929).

[14] R. G. Gordon, J. Chem. Phys. 44, 1830 (1966).

[15] Y. Leroy, E. Constant, and P. Desplanques, J. Chim. Phys. 64, 1499 (1967).

[16] G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, N. J., 1950).

[17] M. E. Baur and W. R. Salzmann, Phys. Rev. Letters 16, 701 (1966), and 18, 590 (1967), and Phys. Rev. 151, 710 (1966).

[18] C. K. Chau, M. V. Klein, and B. Wedding, Phys. Rev. Letters 17, 521 (1966).

[19] B. Keller and F. K. Kneubühl, to be published.

DYNAMICS OF EXCITED-STATE ANNIHILATION IN $NdCl_3$

W. D. Partlow
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

(Received 21 May 1968)

Two processes are observed in $NdCl_3$ whereby two excited Nd^{3+} ions undergo a transition leaving one ion in a higher excited state and the other in a lower state. In one case the initial states are the same, namely ${}^4F_{3/2}$; in the other they are different, ${}^4F_{3/2}$ and ${}^4I_{15/2}$. In both cases fluorescence decays of initial and final states are measured, allowing the determination of the rate equation for the processes.

A number of recent papers[1-6] have been concerned with processes whereby two ions in excited states annihilate, leaving one of the ions in a higher excited state and the other in a lower state. The evidence for such processes is the emission of light from single-ion excited states at energies much more than kT greater than the excitation energy, or the generation of free charge carriers. When the efficiency of the process is relatively high, a change is observed in the decay of the states involved.[5,7] The emission from higher excited states can also result from simultaneous and sequential two-photon absorption of the excitation by single ions.[8] It is necessary to perform fluorescence decay studies or to carry out careful wavelength determinations[2] in order to ascertain which of the processes is important.

This Letter reports determination of the rate equations for two processes of Nd^{3+} in $NdCl_3$, one in which an ion in W annihilates with an ion in R and another in which two ions in R annihilate. The energy levels[9-12] of Nd^{3+} and their spectroscopic notation are shown in Fig. 1.

I. The rate equations.— The lowest order rate equations which can describe excited-state annihilation are given, for pulsed excitation, by

$$\frac{dN_1}{dt}=-\frac{N_1}{\tau_1}-\gamma_{12}N_1N_2+\gamma_{34}N_3N_4, \tag{1}$$

$$\frac{dN_2}{dt}=-\frac{N_2}{\tau_2}-\gamma_{21}N_2N_1+\gamma_{34}N_3N_4, \tag{2}$$

$$\frac{dN_3}{dt}=-\frac{N_3}{\tau_3}+\gamma_{12}N_1N_2-\gamma_{34}N_3N_4, \tag{3}$$

$$\frac{dN_4}{dt}=-\frac{N_4}{\tau_4}+\gamma_{12}N_1N_2-\gamma_{34}N_3N_4; \tag{4}$$

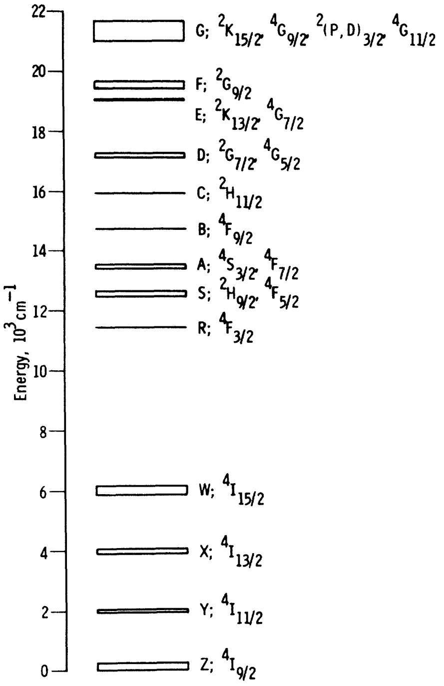

FIG. 1. Energy levels of Nd^{3+}.

N_i are the populations of the states. Figure 2 schematically represents this process, denoted by $1+2\rightarrow 3+4$. γ_i are the lifetimes of the states under resonant excitation in the limit of low population.

These equations do not entirely accout for other processes, both radiative and nonradiative, between the states. The definition of τ_i as being the experimental lifetimes accounts for the effects of these processes upon their initial states. The effects of these processes upon their final states is found to be of no consequence in the present experiments; these will be discussed for the individual cases.

Terms in the rate equations involving higher powers of N_1 and N_2 could also result in annihilation processes. These were not included since the lowest order equations were found to explain the data.

Evidence in the present study indicates that the efficiencies of the processes are low, so that to a good approximation,

$$\frac{dN_i}{dt}=-\frac{N_i}{\tau_i};\; N_i=N_i(0)\exp(-t/\tau_i),\quad i=1,2. \tag{5}$$

In the case that the level 4 is the ground state, the term

$$\gamma_{34}N_3N_4$$

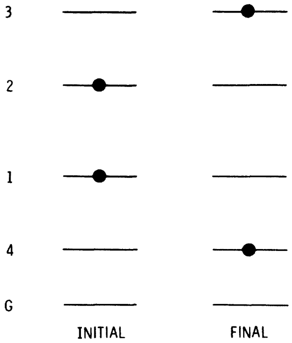

FIG. 2. Illustration of levels for rate equations. Level G represents the ground state.

should not be present in Eq. (3) since this rate is included in the definition of τ_3, depletion of the ground state being neglected. When state 4 is not the ground state this term should be small for low-efficiency processes, so that in either case,

$$dN_3/dt=-N_3/\tau_3+\gamma_{12}N_1N_2,$$

$$N_3=\frac{\gamma_{12}N_1(0)N_2(0)}{1/\tau_3-1/\tau}\left[\exp\left(-\frac{t}{\tau}\right)-\exp\left(-\frac{t}{\tau_3}\right)\right], \tag{6}$$

$$1/\tau=1/\tau_1+1/\tau_2.$$

Equation (6) represents delayed emission from state 3 under pulsed excitation of levels 1 and 2.

For simultaneous and sequential two-photon absorption of pulsed excitation, state 3 would have a single exponential decay with lifetime τ_3.

II. R-W Annihilation.—At 4.2°K emission is observed from D at 16 820 and 15 000 cm^{-1} as well as from R at 9350 cm^{-1} and W at 5750 cm^{-1} when pumping a NdCl$_3$ polycrystalline ingot sample in the region of 10 000 to 14 000 cm^{-1}. The absorptions of R, S, and A fall in this region. An EG & G FX-6B flash lamp fired at 1.5 J was focused on the sample with $f/\frac{1}{2}$ optics; Corning CS7-69 and CS1-69 filters were used to select the excitation wavelengths and to reduce stray light. The light-pulse width was about 10 μsec and the repetition rate 1 sec^{-1}. W is populated via an ion-pair relaxation process by which an ion in S decays directly into two ions in W.[13] The emissions from D, R, and W were detected with S-20 photomultiplier, S-1 photomultiplier, and uncooled Kodak type-N PbS detectors, respectively. Detected wavelengths were selected with $\frac{1}{2}$- and $\frac{1}{4}$-m Jarrell-Ash monochromators in conjunction with narrow-band interference filters. The excitation was flashed repetitively and the signals were averaged on a Princeton Applied

Research Corp. TDH-9 Waveform Eductor. Under these conditions the decays of R and W were exponential with lifetimes of 161 μsec ± 5 % and 1985 μsec ± 5 %, respectively.[3,13-16] The D emission decayed with a lifetime of 139 μsec ± 5 %.[17] Under resonant excitation the lifetime of D was measured to be less than 3 μsec, so the decay time of D when pumping R and W agrees with the value of 149 μsec ± 5 % predicted by Eq. (6) for a fast state populated by an R-W annihilation process. The lifetime of R was measured by pumping resonantly with a monochromatic interference filter and was found to be 167 μsec ± 5 %. This is equal within experimental error to the R lifetime under annihilation conditions and indicates that the process is too inefficient to affect the decay of the R level.

Application of the approximations made in Sec. I is justified for this process. R-W nonradiative transfer is small since the energy gap is too large for phonon relaxation[18] and since no concentration quenching of R is observed at these temperatures.[14] Radiative branching of $R \to W$ has been measured in $LaCl_3$ to be about 0.4 %.[3] Radiative or nonradiative cascading from D to R and W would not be detectable in these experiments because of the low efficiency of the annihilation process.

The agreement of the D decay to the R-W process is not very sensitive to the W lifetime. An experiment was performed in which this parameter could be extracted directly with more accuracy. Utilizing the fact that the W lifetime is much longer than R or D and that W is left with an appreciable population after these other states have decayed, a second flash lamp of variable decay after the firing of the first lamp was used to pump R and not W. A Corning CS7-56 along with the CS7-69 was used for the wavelength selection, the second lamp being imaged on the sample through the envelope of the first lamp. A gate synchronized to the second lamp was open for photomultiplier pulses for 500 μsec after its firing. The number of photons emitted from D in this interval was found to decrease exponentially with delay time after the first flash; the "lifetime" for this decay was measured to be 2003 μsec ± 7 %. This is equal within experimental error to the W lifetime, behaving as predicted by a time integration of Eq. (6).

An investigation was conducted to determine if any of the other states which might have been populated by the flash could account for the delayed D emission and the results of the double flash experiment. All processes including up to four ions were examined using the lowest order rate equations and the values of the lifetimes that have been measured[3,13] or can be estimated by extrapolating $LaCl_3$:Nd^{3+} concentration dependences. The only possibility found in this way is

$$R + Y + Y + Y \to D + Z + Z + Z.$$

This process would require the coincidence of the Y lifetime being 6009 μsec ± 7 %. No value for this lifetime is available, but because of the good agreement of the data with the R-W annihilation model and the high order of alternative models it is felt that the data establish the process to be

$$R + W \to D + Z.$$

The sum of the energies of the lowest R and W crystal-field levels is about 200 cm^{-1} greater than the lowest crystal-field level of D and falls near the highest crystal-field components of this level.

III. <u>R-R Annihilation</u>.–At 77°K, D emission is observed to decay with a lifetime of 89.3 μsec ± 5 % when pumping between 10 000 and 14 000 cm^{-1}. The lifetime of R at this temperature is 181 μsec ± 5 %, so that the D lifetime satisfies Eq. (6) for R-R annihilation. By similar reasoning as used in the previous section, all other possible annihilation processes may be eliminated with the exception of high-order processes involving Y. The only energy matches for R-R annihilation which miss being exact by less than 260 cm^{-1}, the maximum $NdCl_3$ phonon energy,[19] are the following:

$$R + R \to D + W,$$

$$R + R \to E + X,$$

$$R + R \to G + Y.$$

In these cases the processes would require the absorption of from 80 to 160 cm^{-1} of energy from the lattice to conserve energy. This is consistent with the fact that there is no evidence for R-R annihilation at 4.2°K. The decay of both R and D are exponential, indicating that the efficiency of the process is low and that the approximations of Sec. I are valid.

IV. <u>Discussion</u>.–These studies explain the decay of the final states in terms of measured decay characteristics of the initial states by means of a simple set of rate equations. This does not yield much information about the mechanisms of the transfer. Evidence for strong ion-ion interactions and subsequent high migration rates[20,3] in concentrated systems suggests that the processes are of the type described by Dexter.[21] The present experiments cannot distinguish this from the process whereby spontaneous emission is absorbed by ions in excited states. Experiments are planned to study this and other aspects of the effect.

The author wishes to express appreciation to Dr. J. Murphy and Dr. R. W. Warren for many helpful discussions and suggestions.

---

[1] V. V. Ovsyankin and P. P. Feofilov, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 3, 494 (1966), and 4, 471 (1966) [translations: JETP Letters 3, 322 (1966), and 4, 317 (1966)]; P. P. Feofilov and V. V. Ovsyankin, Appl. Opt. 6, 1828 (1967).

[2] M. R. Brown and W. A. Shand, Phys. Letters 18, 95 (1965); R. J. Woodward, J. M. Williams, and M. R. Brown, Phys. Letters 22, 435 (1966).

[3] William B. Gandrud, Technical Report, U. S. Army Research Office Contract No. DA-31-124-ARO-D-339 (1968); William B. Gandrud and H. W. Moos, to be published.

[4] N. A. Tolstoi and A. P. Abramov, Opt. i Spektroskopiya 20, 496 (1966), and 22, 501 (1967) [translations: Opt. Spectry. (USSR) 20, 273 (1966), and 22, 272 (1967), and Fiz. Tverd. Tela 9, 340 (1967) [translation: Soviet Phys.—Solid State 9, 255 (1967)].

[5] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters 10, 400 (1963).

[6] M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, Phys. Rev. Letters 10, 12 (1963).

[7] Joseph Murphy and F. M. Ryan, Bull. Am. Phys. Soc. 13, 415 (1968).

[8] S. Singh and J. E. Geusic, in Optical Properties of Ions in Crystals, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1966), p. 493.

[9] E. H. Carlson and G. H. Dieke, J. Chem. Phys. 34, 1602 (1961).

[10] F. Varsanyi and G. H. Dieke, J. Chem. Phys. 33, 1616 (1960).

[11] G. A. Prinz, dissertation, Johns Hopkins University, 1966 (unpublished).

[12] Energies for $NdCl_3$ levels when not avaiable in Ref. 11 were extrapolated from the low-concentration data of Ref. 9 on the basis of a systematic shift of the optical levels by 0.08% to lower energies.

[13] W. D. Partlow and H. W. Moos, Phys. Rev. 157, 252 (1967).

[14] C. K. Asawa and M. Robinson, Phys. Rev. 141, 251 (1966).

[15] G. E. Barasch and G. H. Dieke, J. Chem. Phys. 43, 988 (1965).

[16] The lifetimes of R and W in these measurements are in fair agreement with previous measurements given in Refs. 3, 13, and 14, although those measured here are consistently shorter. Gandrud and Moos have shown that migration to trace impurities strongly affects the lifetimes of rare-earth infrared states and leads to variation from sample to sample. Barasch and Dieke have attributed other such variations to resonance radiation trapping.

[17] It is difficult to rule out the presence of faster decay components at early times since a small amount of scattered pump light reaches the detector. If present, however, the intensity of these components is never greater than 10% of the main component.

[18] L. A. Riseberg and H. W. Moos, Phys. Rev. Letters 19, 1423 (1967).

[19] E. Cohen and H. W. Moos, Phys. Rev. 161, 258 (1967).

[20] L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin, J. Chem. Phys. 45, 1578 (1966).

[21] D. L. Dexter, Phys. Rev. 126, 1962 (1962).

---

rf-INDUCED SIDEBANDS IN MÖSSBAUER SPECTRA[*]

Neil D. Heiman,[†] Loren Pfeiffer, and J. C. Walker[‡]
Physics Department, Johns Hopkins University, Baltimore, Maryland

(Received 8 April 1968)

We report the first clear evidence that rf magnetic fields generate acoustical sidebands in the Mössbauer spectra of metallic Fe^{57}. We advance an explanation of this magnetoacoustic effect in terms of magnetostriction, and suggest that this effect provides a consistent explanation of the results of several earlier workers who observed rf resonance effects seemingly associated with hyperfine transitions.

Additional distinct lines in the Mössbauer absorption of metallic Fe^{57} have been generated by subjecting the iron absorber foil to an rf magnetic field. These additional lines are interpreted as acoustically modulated sidebands arising from magnetostrictive effects within the iron. It should be emphasized that the present experiments do not involve an absorber fastened to a piezoelectric oscillator, but deal with internal vibrations in the absorber itself.

The influence of rf magnetic fields on Mössbauer spectra was first investigated by Perlow,[1] who observed a change in recoilless absorption at 25.98 MHz, the hyperfine resonant frequency