

## Direct Evidence for and Transition Rates of Ion-Pair Interactions in $\text{LaCl}_3 : \text{Ho}^{3+}$ †

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(Received 7 March 1966; revised manuscript received 13 July 1966)

Energy transfer between  $\text{Ho}^{3+}$  ions in a  $\text{LaCl}_3$  lattice has been studied by means of relative fluorescence intensity measurements. By careful measurements of the relative fluorescence from  $E(^5S_2)$ ,  $C(^5I_4)$ , and  $Y(^5I_7)$  it was demonstrated that to within the experimental error,  $E$  relaxes to  $C$  only by an ion-pair process. The concentration dependence of the pair process is linear. Assumption of a simple model with a sharp radial dropoff led to an effective range of 7.5 Å (third-nearest neighbor) for the ion-pair interaction.

### I. INTRODUCTION

THE transfer of energy between metastable excited states of ions in crystals by the ion-pair or resonance process has been studied in a number of rare-earth-rare-earth and transition-metal-rare-earth systems since first observed by Varsanyi and Dieke<sup>1</sup> in  $\text{Er}^{3+}$ . In general this process will occur whenever two excited (metastable) states of an ion, ion  $A$ , differ by an energy equal to or slightly greater than the energy of an excited state of another ion, ion  $B$ . In this process ion  $A$  decays from the upper excited state to the lower excited state by exciting ion  $B$  to an appropriate excited level, energy being conserved by the emission of a phonon if necessary. Ions  $A$  and  $B$  may be similar or dissimilar.

Previous studies of the pair process have largely been based on the quenching of fluorescence of ion  $A$  as a function of certain parameters of ion  $B$ . These parameters may be the concentration of ion  $B$ , the degree of energy match afforded by ion  $B$ , or the number of transitions of ion  $B$  affording a suitable match for a decay of ion  $A$ .

Peterson and Bridenbaugh have studied the pair process for<sup>2,3</sup>  $\text{Tb}^{3+}$  and<sup>4</sup>  $\text{Nd}^{3+}$  including self-quenching and quenching by other rare-earth ions. Specifically in the self-quenching case they note a rise time of the lower excited state ( $^5D_4$ ) for  $\text{Tb}^{3+}$  consistent with the decay time of the upper state ( $^5D_3$ ). For  $\text{Nd}^{3+}$  they note a decrease in the lifetime of the upper state ( $^4I_{15/2}$ ) as a function of  $\text{Nd}^{3+}$  concentration. This decrease is essentially linear over a range of concentration

from 3% to ~50% with a departure from linearity at lower concentrations. We return to this result for comparison purposes.

Kiss<sup>5</sup> has studied the transfer of energy from  $\text{Cr}^{3+}$  to  $\text{Nd}^{3+}$ . There is a near match between the  $^2E$  level of  $\text{Cr}^{3+}$  and one of the levels above the  $^4F_{3/2}$  level of  $\text{Nd}^{3+}$  followed by a subsequent decay to the  $^4F_{3/2}$  level. From the study of the lifetimes of the  $E^2$  level of  $\text{Cr}^{3+}$  and  $^4F_{3/2}$  level of  $\text{Nd}^{3+}$  singly and as co-dopants he deduces a cross-transfer rate of the order of  $10^8 \text{ sec}^{-1}$ .

It is the purpose of this paper to examine the process of energy transfer between similar ions directly, using relative fluorescence intensity measurements and con-

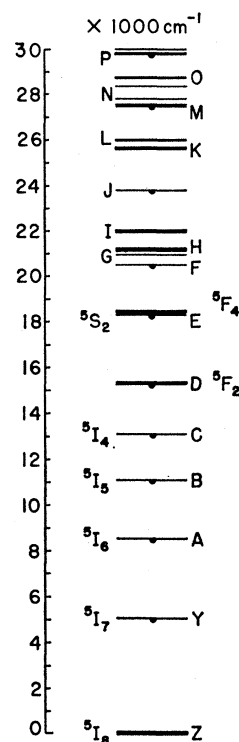


FIG. 1. Energy levels of  $\text{Ho}^{3+}$  in  $\text{LaCl}_3$  below  $30\,000 \text{ cm}^{-1}$ . The levels connected by pair transitions are  $M \rightarrow I$ ,  $K \rightarrow F$ ,  $J \rightarrow E$ ,  $F \rightarrow D$ , and  $E \rightarrow C$ .

† Work supported by U. S. Army Research Office (Durham).

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<sup>1</sup> F. Varsanyi and G. H. Dieke, *Phys. Rev. Letters* **7**, 442 (1961).

<sup>2</sup> G. E. Peterson and P. M. Bridenbaugh, *J. Opt. Soc. Am.* **53**, 301 (1963).

<sup>3</sup> G. E. Peterson and P. M. Bridenbaugh, *J. Opt. Soc. Am.* **53**, 1129 (1963).

<sup>4</sup> G. E. Peterson and P. M. Bridenbaugh, *J. Opt. Soc. Am.* **54**, 644 (1963).

<sup>5</sup> Z. J. Kiss, *Phys. Letters* **13**, 654 (1964).

ervation of energy rather than lifetime measurements. For the case of dissimilar ions, the presence of fluorescence from ion  $B$  when ion  $A$  is excited is sufficient evidence for the pair process,<sup>5</sup> but such is not the case for similar ions where other transfer processes are possible. Specifically for  $\text{Ho}^{3+}$  in  $\text{LaCl}_3$ , it will be shown that the ion-pair process is the only significant process involved in the transfer of energy between the excited states  ${}^5S_2$  and  ${}^5I_4$  when the former is excited. In addition, the transition rate has been measured for the pair process in a 3.5% sample and found to be comparable to the radiative rates from the  ${}^5S_2$  to the  ${}^5I_8$  and  ${}^5I_7$  states. The concentration dependence of this transition rate has been studied and will be discussed on the basis of the theoretical model proposed by Dexter<sup>6</sup> and Dexter and Schulman.<sup>7</sup>

## II. ENERGY TRANSFER IN $\text{LaCl}_3:\text{Ho}^{3+}$

Dieke and Pandey<sup>8</sup> have shown that there are four pairs of levels separated by the energy difference between the ground state and the first excited state, and excitation of the higher of the two always produces fluorescence from the lower but not from any intervening levels. Referring to Fig. 1 (taken from Dieke and Pandey), these pairs are  $M \rightarrow I$ ,  $K \rightarrow F$ ,  $J \rightarrow E$ , and  $F \rightarrow D$ . Recent work<sup>9</sup> has shown that levels  $A$ ,  $B$ , and  $C$  also fluoresce and that  $C$  fluorescence is produced by  $E$  excitation, presenting a fifth pair of levels separated by the energy of the first excited state,  $Y$ ,  $\sim 5000 \text{ cm}^{-1}$  and behaving as above. It should be noted that there are several possibilities for a cascading process by successive ion-pair transitions,  $K$  going to  $F$ , and  $F$  then to  $D$ , likewise  $J \rightarrow E$ , followed by  $E \rightarrow C$ .  $F$  is also "fed" by  $M$  since  $I$  relaxes to  $F$  by a multiphonon emission process.

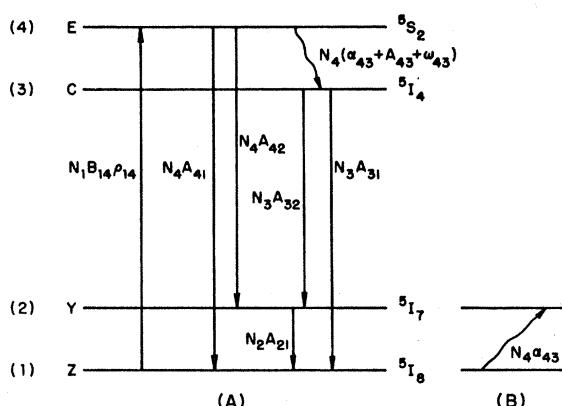


FIG. 2. Energy levels of  $\text{Ho}^{3+}$  relevant to the  $E \rightarrow C$  pair transition with transitions for rate equations indicated.

<sup>6</sup> D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

<sup>7</sup> D. L. Dexter and J. H. Schulman, J. Chem. Phys. **22**, 1063 (1964).

<sup>8</sup> G. H. Dieke and B. Pandey, J. Chem. Phys. **41**, 1952 (1964).

<sup>9</sup> J. F. Porter, Jr., dissertation, The Johns Hopkins University, 1966 (unpublished).

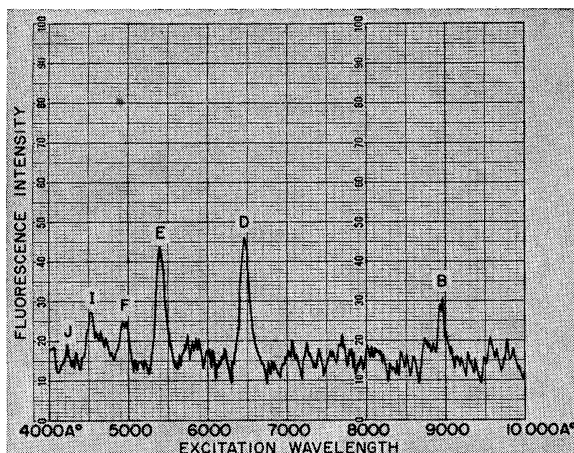


FIG. 3. Fluorescence excitation spectrum of the ( ${}^5I_6$ )  $A$  level.

Of the five pairs of levels coupled by the ion-pair process the lowest pair,  $E$  and  $C$ , was deemed best for an initial study since there are fewer possible transitions. The nearly exact energy match leads to a simplified no-phonon decay scheme. The energy levels and significant transitions are shown in Fig. 2. The steady-state rate equations for levels 3( $C$ ) and 2( $Y$ ) are then given by

$$\dot{N}_3 = N_4(\alpha_{43} + \omega_{43} + A_{43}) - N_3(A_{32} + A_{31}) \equiv 0, \quad (1)$$

$$\dot{N}_2 = N_4A_{42} + N_3A_{32} + N_4\alpha_{43} - N_2A_{21} \equiv 0, \quad (2)$$

where the  $A_{ij}$  are the Einstein coefficients for spontaneous emission,  $\alpha_{43}$  is the transition probability for the decay from 4( $E$ ) to 3( $C$ ) by the pair process, and  $\omega_{43}$  is the transition probability for decay via the lattice (multiphonon emission). There are other possible multiphonon transitions but their probabilities are assumed to be of the same order as  $\omega_{43}$  which will be shown to be negligible. No terms are included in the rate equations for reabsorption processes since most of the radiative transitions involved terminate at levels above the ground state. Under the experimental conditions the population of these levels is insufficient to cause observable reabsorption.

It is first necessary to justify that this simplified scheme is valid, particularly that levels  $A$  and  $B$  do not contribute to the population of the  $Y$  state when the  $E$  level is excited and that Eq. (2) does indeed include all significant methods of populating level 2( $Y$ ). The excitation spectra of levels  $A$  and  $B$  are shown in Figs. 3 and 4 and both are seen to be only very weakly excited by  $E$  excitation. A search was made for a radiative transition from  $E$  to  $A$  and none was found. Both  $A$  and  $B$  excitation can be explained by pair process involving  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$  impurities, both known to be present. On this basis the contribution of levels  $A$  and  $B$  to the population of  $Y$ , with  $E$  excitation, is neglected.

Another simplification can be made, that is,  $\omega_{43}$  may

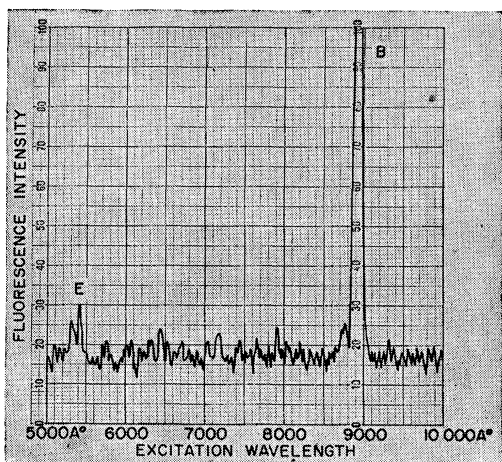


FIG. 4. Fluorescence excitation spectrum of the ( ${}^6I_5$ )  $B$  level.

be neglected. Multiphonon transitions in rare earths for energy gaps of this magnitude ( $\sim 5000 \text{ cm}^{-1}$ ) are generally negligible as can be seen from the study of lifetimes by Barasch and Dieke.<sup>10</sup> In addition the excitation spectrum of the  $C$  level, shown in Fig. 5, indicates that there is no  $D$  excitation of  $C$  fluorescence and hence no multiphonon transition from  $D$  to  $C$ . If there were a multiphonon transition from  $E$  to  $C$  previous experience indicates that there would be such a transition from  $D$  also. On this basis the term  $\omega_{43}$  is neglected.

The term  $A_{43}$  is neglected for the following reasons. This term, accounting for  $E$  to  $C$  fluorescence, should lead to a group of lines just to the short wavelength side of the  $Y$ - $Z$  group. Examination of the infrared fluorescence spectrum under broad-band excitation shows that if there is any  $E$ - $C$  fluorescence it is certainly less than one-thirtieth of the intensity of the strongest lines in the  $Y$ - $Z$  group. A search was also made for a radiative  $J \rightarrow E$  transition which would be much further removed from the  $Y$ - $Z$  transition due to the energy mismatch. No such radiative transition was found in this case either. On the basis of these two observations the term in  $A_{43}$  is neglected. Furthermore, the experimental results justify these assumptions to within experimental error.

Rewriting the rate equations in terms of fluorescence intensities, Eqs. (1) and (2) are

$$I_{43}' \cong N_4 \alpha_{42} = N_3 (A_{32} + A_{31}) = I_{32} + I_{31} = I_{CY} + I_{CZ}, \quad (3)$$

$$I_{43} = N_4 \alpha_{43} = N_2 A_{21} - N_4 A_{42} - N_3 A_{32} \\ = I_{21} - I_{42} - I_{32} = I_{YZ} - I_{CY} - I_{EY}. \quad (4)$$

$I_{43}'$  is the relative transition rate from 4 to 3 by any process, and  $I_{43}$  is the relative transition rate from 1 to 2 by the ion-pair process alone. If the two can be shown to be equal experimentally, then the ion-pair process is established as the only mechanism for decay. Further-

<sup>10</sup> G. E. Barasch and G. H. Dieke, J. Chem. Phys. 43, 988 (1965).

TABLE I. Results of intensity measurements.

Transition	Wave-length $\mu$	Relative sensitivity photon $\text{sec}^{-1} \text{ mV}^{-1}$	Signal	Relative intensity photons $\text{sec}^{-1}$
$E \rightarrow Y$	0.754	$9.26 \pm 1.0$	$5.66 \pm 0.12(3)$	$53 \pm 6.8$
$C \rightarrow Y$	1.250	$3.79 \pm 6$	$0.186 \pm 0.008$	$70.5 \pm 4.2$
$C \rightarrow Z$	$\sim 0.755$	$9.36 \pm 1.0$	0.6	$5.6 \pm 0.5$
$Y \rightarrow Z$	$\sim 2.000$	$2.70 \pm 0$	$0.770 \pm 0.017$	$208 \pm 4.6$

more the ratio of the inferred pair transition rate to the measured rate from  $E$  to  $Y$  ( $I_{EY}$ ) gives the relative transition probability for the pair process.

### III. EXPERIMENTAL RESULTS

The fluorescence intensities of the relevant transitions were measured with an  $\sim f/3.3$  modified Czerny-Turner spectrometer using a Bausch and Lomb grating blazed at  $1.6 \mu$ . A beam-switching mirror at the exit slit allowed the use of either an S-20 photomultiplier (EMI 9558 QA) or a PbS detector (Ektron N-2) cooled with dry ice. Excitation was obtained from a G.E. AH-6 high-pressure mercury lamp and a Bausch and Lomb 500 mm monochromator. Suitable filtering was used to eliminate stray light. A powdered sample was used to avoid polarization effects and was made from a 3.5%  $\text{Ho}^{3+}:\text{LaCl}_3$  single-crystal ingot. The powder was sealed in a quartz tube partially filled with  $\sim \frac{1}{2}$  atm of helium gas and cooled by immersion in liquid helium.

The system was calibrated at the relevant wavelengths using an uncalibrated NBS test lamp powered from a constant current source. The temperature of the tungsten ribbon was measured with a Leeds and Northrup optical pyrometer and corrections applied for brightness temperature and emissivity. The nominal wavelengths involved were  $0.654 \mu$ ,  $1.25 \mu$ , and  $2.00 \mu$ .

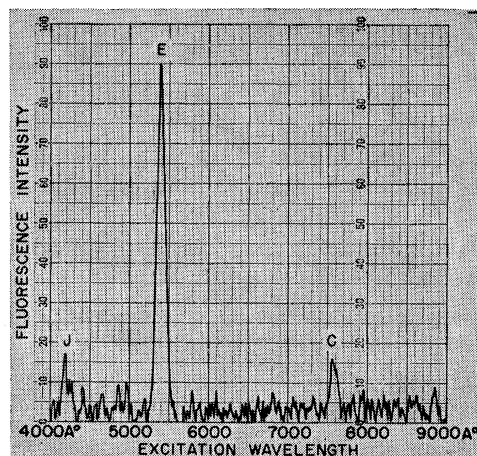


FIG. 5. Fluorescence excitation spectrum of the ( ${}^6I_4$ )  $C$  level.

which necessitated the cross calibration of the two detectors in a relative sense. The over-all system sensitivity was determined in terms of photons  $\text{sec}^{-1} \text{mV}^{-1}$ .

The results are summarized in Table I. Inserting these values in Eqs. (3) and (4), the values for  $I_{43}'$  and  $I_{43}$  are obtained:

$$I_{43}' = I_{CY} + I_{CZ} = 76.6 \pm 4.5 \text{ sec}^{-1}, \quad (5)$$

$$I_{43} = I_{YZ} - I_{CY} - I_{EY} = 84 \pm 16 \text{ sec}^{-1}, \quad (6)$$

establishing that to within experimental error ( $\pm 20\%$ ) the two values are equal. Thus the ion-pair process is established as the decay mechanism, and in addition radiative and lattice effects are shown to be negligible within experimental error.

The importance of this measurement lies in the fact that it gives a direct measurement of the transition probability of the pair process as well as establishing that it is the only significant mechanism for transferring energy from  $E$  to  $C$ .

The relative transition probabilities for the radiative transition from  $E$  to  $Y$  and the pair transition from  $E$  to  $C$  are obtained from the above results:

$$\frac{N_{4\alpha_{43}}}{N_{4A_{42}}} \frac{I_{EC}}{I_{EY}} = 1.49 = \frac{\alpha_{43}}{A_{42}}. \quad (7)$$

The only other significant transition from the  $E$  level is a radiative transition to the ground state  $Z$ . The relative intensities of the  $E$  to  $Z$  and  $E$  to  $Y$  transitions were measured with  $J$  excitation and found to be  $I_{EZ}/I_{EY} = 1.16$ . From these ratios it is easily shown that  $\sim 41\%$  of the ions in the  $E$  level decay to  $C$  via a pair transition. Barasch and Dieke<sup>10</sup> have measured the lifetime of the  $E$  state at  $4.2^\circ\text{K}$  for a  $2\%$   $\text{Ho}^{3+}$  sample and found it to be  $300 \mu\text{sec}$ . Using this value for the lifetime of the  $E$  state and a relative transition probability for the pair process in a  $2.0\%$  sample obtained from the  $3.5\%$  data as explained in the next paragraph, the pair transition rate from  $E$  to  $C$  in  $2.0\%$   $\text{Ho}^{3+} \text{LaCl}_3$  is  $\sim 1 \times 10^3 \text{ sec}^{-1}$ .

The relative transition probability for the pair process has been measured at  $4.2^\circ\text{K}$  for samples ranging in concentration from  $0.05$  to  $10.0$  mole%. This was done by measuring the ratio of intensities of the  $C$ - $Y$  and  $E$ - $Y$  transitions assuming the radiative transition probability from  $E \rightarrow Y$  to be a constant. This ratio is proportional to the pair transition probability, the proportionality constant being concentration independent. Powdered samples were used as described previously mostly taken from polycrystalline ingots. The results are given in Fig. 6 showing a linear dependence of the pair-process transition probability on concentration as was observed by Peterson and Bridenbaugh<sup>4</sup> for  $\text{Nd}^{3+}$ . The point spread is largely attributed to variations in concentration since  $\text{Ho}^{3+}$  is not isostructural with  $\text{LaCl}_3$ .

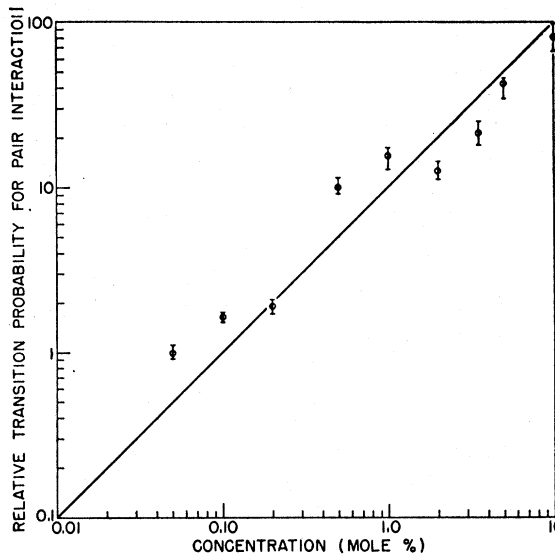


Fig. 6. Concentration dependence of the ion-pair transition rate for the  $E \rightarrow C$  transition at  $4.2^\circ\text{K}$ . The largest source of error is assumed to be in concentration as indicated in the text.

#### IV. DISCUSSION

The theory of sensitized luminescence<sup>6</sup> may be used to describe the ion-pair energy-transfer process. The two pairs of transitions  $E \rightarrow C$ ,  $Z \rightarrow Y$ , and  $E \rightarrow Y$ ,  $Z \rightarrow C$  are energetically equivalent and cannot be distinguished by this experiment. It is not clear which interaction dominates the energy-transfer process. Most of the  $f$ -to- $f$  radiative transitions are electric dipole. Magnetic-dipole transitions are forbidden in the Russel-Saunders limit except within multiplets. Varsanyi and Dieke<sup>11</sup> examined the  $Z_1 \rightarrow Y$  transitions and found that they were given by electric-dipole selection rules. The radial dependence of magnetic dipole and electric-dipole interaction is the same. The effect of exchange<sup>6,12</sup> is not known. Static splitting in ground and excited states due to near and next-nearest rare-earth neighbors have been observed in trichloride lattices.<sup>13</sup> These splittings are larger than can be caused by magnetic-dipole interactions and must be due to exchange. Such information is not available for  $\text{LaCl}_3:\text{Ho}^{3+}$ . Furthermore, the exchange splittings do not give direct information about the pair-transition rates, and this information cannot be used without a more detailed analysis.

Electric dipole-electric quadrupole<sup>6</sup> and electric quadrupole-electric quadrupole<sup>6,14</sup> interactions may become very important when the electric-dipole oscillator strengths are as small as they are in the rare earths. The electric-quadrupole selection rules are  $|\Delta J| \leq 2$  and in the Russel-Saunders limits  $\Delta S = 0$ ,  $|\Delta L| \leq 2$ .

<sup>11</sup> F. Varsanyi and G. H. Dieke, J. Chem. Phys. **36**, 835 (1962).

<sup>12</sup> W. M. Yen, R. L. Greene, W. C. Scott, and D. L. Huber, Phys. Rev. **140**, A1188 (1965).

<sup>13</sup> G. A. Prinz, Phys. Letters **20**, 323 (1966).

<sup>14</sup> J. D. Axe and P. F. Weller, Jr. Chem. Phys. **40**, 3066 (1964).

Only the  $Z \rightarrow Y$  transition is permitted. In intermediate coupling  $Z \rightarrow C$  and  $E \rightarrow Y$  are always forbidden. Only a small amount of  ${}^5G_2$  is expected to be mixed with the  ${}^5S_2$  so that the quadrupole oscillator strength between  $C$  and  $E$  will be small.<sup>15,16</sup> The quadrupole oscillator strengths have not been measured although theoretical estimates have been made.<sup>17,18</sup>

We will show below that reasonable values of the  $E \rightarrow C$  electric dipole oscillator strengths and an electric-dipole-electric-dipole interaction gives values of the transition rate agreeing with the experiment. In view of the fact that  $Z \rightarrow Y$  is allowed as a quadrupole transition, an electrical dipole-electric-quadrupole interaction may be dominant, thus nothing definite can be said about the interaction mechanism until more is known about the various oscillator strengths involved.

Because of the presence of a symmetry axis, polarization rules need be considered for only a few sites. An electric-dipole interaction is of the form

$$\frac{e^2}{n^2 R^3} \left\{ \mathbf{r}_{ij^s} \cdot \mathbf{r}_{i'j'^a} - \frac{3}{R^2} (\mathbf{r}_{ij^s} \cdot \mathbf{R})(\mathbf{r}_{i'j'^a} \cdot \mathbf{R}) \right\}. \quad (8)$$

$\mathbf{r}_{ij^s}$  is the expectation value of the electron-nucleus distance between the initial and final states of the sensitizer which is initially excited.  $\mathbf{r}_{i'j'^a}$  is the same quantity for the absorber to which the energy is transferred.  $\mathbf{R}$  is the distance between the atoms and  $n$  is the index of refraction. For certain directions of  $\mathbf{R}$ , specifically when the ions are along the  $z$  axis or in the  $x$ - $y$  plane (next-nearest neighbor and third-nearest neighbor, respectively), both simultaneous transitions must be of the same polarization. The  $E_1^0$  and  $E_2^0$  levels are at 18 429.3  $\text{cm}^{-1}$  and 18 432.1  $\text{cm}^{-1}$ . The next level is 82.4  $\text{cm}^{-1}$  higher and need not be discussed further. Examination of the sum of the energies of the Stark components of  $C$  and  $Y$  indicates that  $C_3+Y_5$ ,  $C_3+Y_6$ ,  $C_4+Y_5$ ,  $C_4+Y_6$ ,  $C_5+Y_1$ , and  $C_5+Y_2$  (other pairs of levels may overlap if they have sufficient breadth) are within 3  $\text{cm}^{-1}$  of these energies. In both cases of  $E \rightarrow Y$ ,  $Z \rightarrow C$ , and  $E \rightarrow C$ ,  $Z \rightarrow Y$ , transitions of the same polarization are permitted. In this particular case selection rules do not forbid transitions to the specially positioned sites and in lieu of more quantitative information we average over all directions to obtain

$$\frac{2}{3} \frac{e^2}{n^2 R^2} |\mathbf{r}_{ij^s}|^2 |\mathbf{r}_{i'j'^a}|^2. \quad (9)$$

Equation (9) of Ref. 6 may then be rewritten in terms of the oscillator strength. The transition rate due to

<sup>15</sup> M. H. Crozier and W. A. Runciman, J. Chem. Phys. **35**, 1392 (1961).

<sup>16</sup> H. M. Crosswhite (private communication).

<sup>17</sup> L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, Physica **11**, 231 (1945).

<sup>18</sup> C. K. Jorgensen and B. R. Judd, Mol. Phys. **8**, 281 (1964).

electric-dipole coupling

$$P_{sa}(dd) = \frac{3e^4}{8\pi^2 m^2 c^3} \frac{1}{n^4 R^6 \bar{\nu}^2} \times \sum_{jj'} \left[ f_{ij^s} f_{i'j'^a} \int F_{ij^s}(\bar{\nu}) F_{i'j'^a}(\bar{\nu}) d\bar{\nu} \right]. \quad (10)$$

The oscillator strengths  $f_{ij^s}$  and  $f_{i'j'^a}$  are those for the ion in a vacuum. Index of refraction and local field effects must be accounted for when computing them from absorption or lifetime data. The line-shape function  $F_{ij^s}(\bar{\nu})$  are normalized to give unity when a single one is integrated over  $\bar{\nu}$ . For perfect overlap and identical linewidth, the product integral  $\sim \Delta\bar{\nu}^{-1}$ . Although the rare-earth interactions are quite small, the linewidths are quite narrow, from 0.03  $\text{cm}^{-1}$  to 10  $\text{cm}^{-1}$ , concentrating the intensity so that pair interactions may take place at a significant rate when the overlap is not too small. The role of phonons may be treated phenomenologically by the  $F_{ij^s}(\bar{\nu})$ .

The question of energy migration must now be treated. The average distance between  $\text{Ho}^{3+}$  ions in a 3.5% concentration crystal is 15 Å. The lifetime of  $E^0$  at 4.2°K is about  $3 \times 10^{-4}$  sec. The radiative transition rates for  $E \rightarrow Y$  and  $E \rightarrow Z$  are approximately equal. The only energetically permitted transitions for excitation migration are  $E_1^0$  and  $E_2^0$  to  $Z_1$  and vice versa. Electric-quadrupole transitions are forbidden between  $E$  and  $Z$ . Examination of a 1%  $\text{Ho}^{3+}$  in  $\text{LaCl}_3$  spectral plate indicates that the  $E_1^0$  and  $E_2^0$  to  $Z_1$  intensity is less than 5% of the total  $E_1^0$  and  $E_2^0$  to  $Z$  intensity.  $n$  was determined to be 1.56. Using a cubic field approximation for the effective field,  $f \leq 1 \times 10^{-7}$ . Assuming the oscillator strength is divided evenly between the two transitions, and the overlap integrals have a value  $\sim (1 \text{ cm}^{-1})^{-1}$ , the transition rate for a 15-Å separation is  $\leq 20 \text{ sec}^{-1}$ , much less than the decay rate of  $E$ .

The interaction has a very strong radial dependence and for simplicity an essentially square-well model is assumed. It is assumed that the interaction has a critical radius  $r_c$  such that if one or more  $\text{Ho}^{3+}$  ions are within this distance of an excited  $\text{Ho}^{3+}$  ion, the pair relaxation will take place. For  $r_i > r_c$  the interaction is assumed to be negligible.

The probability of one or more  $\text{Ho}^{3+}$  ions being within a radius  $r_c$  about an excited  $\text{Ho}^{3+}$  ion is

$$1 - (1 - C)^{N_c} \quad (11)$$

where  $C$  is the concentration of  $\text{Ho}^{3+}$  ions and  $N_c$  is the number of sites within  $r_c$ . The La ions are arranged in the  $\text{LaCl}_3$  lattice such that these are 2 neighbors at  $\sim 4.4$  Å, 6 at  $\sim 5.0$  Å, and 6 at 7.5 Å. For  $N_c = 14$  and  $C = 0.035$ , the probability is 0.39 which corresponds to the measured fraction of 0.41. This indicates that the interaction must extend out to at least third-nearest neighbor at 7.5 Å and is a fairly long-range interaction.

The pair transition rate can be estimated. Consider

$E_1^0, E_2^0 \rightarrow C$ , and  $Z_1 \rightarrow Y$ . The allowed electric-dipole transitions which conserve energy are to  $C_3+Y_5$ ,  $C_3+Y_6$ ,  $C_4+Y_5$ , and  $C_4+Y_6$ . Using the results of Varsanyi and Dieke for  $Z_1 \rightarrow Y_5, Y_6$  corrected for index of refraction and local field effects (a cubic field approximation and visible value of  $n$  were used) and an overlap integral for each pair of levels of  $1/(3 \text{ cm}^{-1})$ , Eq. (10) yields a rate of  $1 \times 10^8 \text{ sec}^{-1}$  at  $7.5 \text{ \AA}$  if the oscillator strengths to  $C_3$  and  $C_4$  are each  $3 \times 10^{-8}$ . Such oscillator strengths are reasonable.

It is not possible, then, to ascertain the nature of the ion-pair interaction. Although electric dipole-electric quadrupole or electric quadrupole-electric quadrupole interactions are expected, reasonable values of the  $E \rightarrow C$  electric-dipole oscillator strength give the transition rate. For this reason, better estimates of the oscillator strengths involved must be obtained before the type of interaction can be decided.

## V. CONCLUSION

Energy transfer between  $\text{Ho}^{3+}$  ions in a  $\text{LaCl}_3$  lattice has been studied by means of careful fluorescence intensity measurements. Unequivocal direct evidence has been found that  $E$  to  $C$  is a pair transition. The upper limit of radiative and multiphonon rates from  $E$  to  $C$  were found to be much less than the ion-pair rate. In a 3.5% concentration sample of  $\text{LaCl}_3:\text{Ho}^{3+}$ , 41% of the ions in  $E$  decayed to  $C$  via a pair transition. Assuming a simple model this corresponded to an interaction range of at least  $7.5 \text{ \AA}$ . The concentration dependence was linear, agreeing with the model. Adjusting the transition rate for concentration dependence and using the lifetime of the  $E$  state obtained by Barasch and Dieke<sup>10</sup> for a 2% sample a pair transition rate of  $\sim 1 \times 10^8 \text{ sec}^{-1}$  was obtained. It was not possible to ascertain the detailed nature of the interaction.

## Irreversibility in Heisenberg Spin Systems. I. General Formalism and Kinetic Equations in the High-Temperature Limit

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 (Received 13 June 1966)

Starting from the von Neumann equation for the spin density matrix of a Heisenberg system, we analyze the perturbation expansion of the spin autocorrelation function by the diagrammatic technique previously applied to quantum gases. We demonstrate a number of theorems which allow us to express this perturbation series in terms of renormalized graphs only; we then derive a kinetic equation for the autocorrelation function. The main feature of this equation is that the kernel, which is highly nonlinear in the autocorrelation function itself, tends to zero in the limit of long times. The results, which are exact in the high-temperature region and in the Weiss limit (number of neighbors  $Z \rightarrow \infty$ ), allow us to consider the behavior of the autocorrelation function for times both short and long. This model is a typical example of a system with a discrete unperturbed spectrum showing an irreversible behavior.

### I. INTRODUCTION

MODERN development in the  $N$ -body problem has led to considerable progress in the understanding of the equilibrium properties of the Heisenberg spin system.<sup>1,2</sup> A qualitative description is now available that covers the whole range from the low-temperature spin-wave region to the high-temperature paramagnetic region. Moreover, the Heisenberg model also offers the possibility of testing various approximation methods for analyzing the phase transition at the Curie point  $T_c$ .

On the other hand, except in the well-known spin-wave region,<sup>3</sup> very little is known about the nonequilib-

rium behavior of the Heisenberg model. However, this problem has much interest: First, it furnishes a typical example of a dynamical system the dissipative properties of which may not be described by a Boltzmann-like equation; indeed, except again for spin waves, the meaning of the concept of a "collision" between spins cannot be guessed from what is known in other situations. Second, the knowledge of the time behavior of a spin system is essential to analyze the numerous experiments on ferromagnets, among which neutron-scattering measurements take an important place.

In these latter experiments, a central role is played by the so-called spin autocorrelation functions<sup>4</sup>

$$\Gamma_{ab}^{\alpha\beta}(t) = \langle S_a^\alpha(t) S_b^\beta(0) \rangle, \quad (\text{I.1})$$

where  $S_a^\alpha(t)$  denotes the Heisenberg representation of spin component  $\alpha$  ( $\alpha = z, +, -$ ) at lattice point  $a$ , and the

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<sup>1</sup> See, for instance, R. Brout, *Phase Transitions* (W. A. Benjamin and Company, Inc., New York, 1965), Chaps. I, II, V and references quoted therein.

<sup>2</sup> See also D. Mattis, *The Theory of Magnetism* (Harper & Row, New York, 1964).

<sup>3</sup> F. J. Dyson, *Phys. Rev.* **102**, 1217 (1956); **102**, 1230 (1956).

<sup>4</sup> L. Van Hove, *Phys. Rev.* **95**, 1374 (1954).

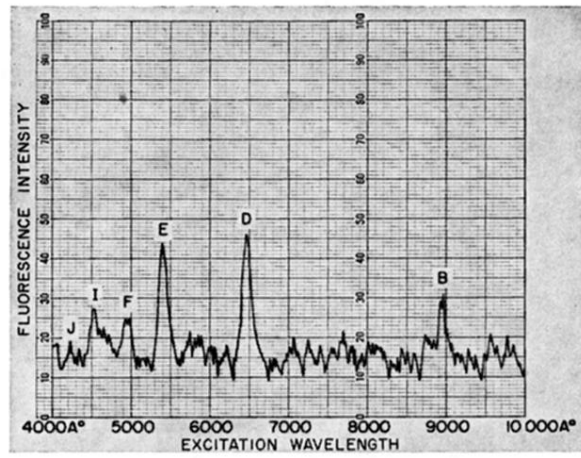


FIG. 3. Fluorescence excitation spectrum of the  $(^6I_6) A$  level.

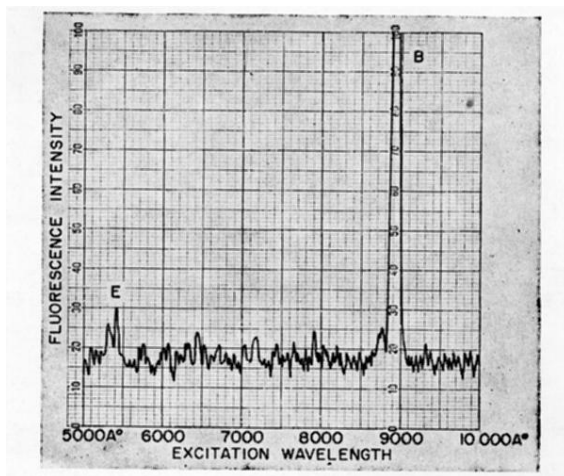


FIG. 4. Fluorescence excitation spectrum of the ( ${}^6I_5$ ) *B* level.



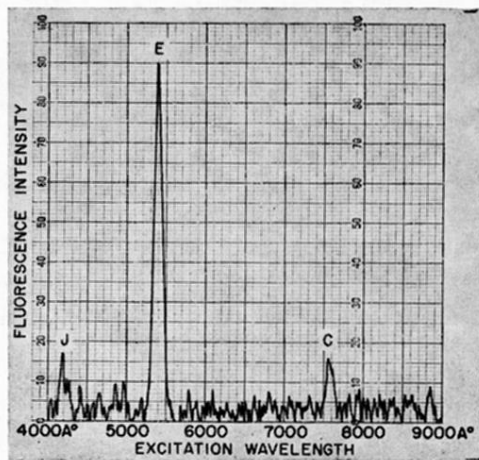


FIG. 5. Fluorescence excitation spectrum of the ( ${}^6I_4$ ) C level.