

N69-35809
NASA CR-105406

THE JOHNS HOPKINS UNIVERSITY

Department of Physics

Baltimore, Maryland 21218

Final Report on

"Investigation of Rare Earth Ions"

NGR 21-001-002

1 March 1963 - 31 July 1969

Total Funding \$245,000

**CASE FILE
COPY**

Personnel

G. H. Dieke	Responsible Investigator to August 1965
H. W. Moos	Responsible Investigator from September 1965
M. Leask	Research Associate
R. Isler	Research Assistant (Summer)
G. Barasch	Research Assistant
Ph. D. 1965 - "Fluorescent Lifetimes of, and Energy Transfer between, Excited States of Rare Earth Ions in Crystals"	
W. Partlow	Research Associate
C. Rector	Research Assistant Research Associate
Ph. D. 1966 - "Electron Paramagnetic Resonance and Optical Spectra of $\text{CaF}_2:\text{Er}^{3+}$ "	
E. Cohen	Research Assistant Research Associate
Ph. D. 1967 - "Vibronic Transitions of Hexagonal Rare Earth Trichlorides"	
B. Kim	Research Assistant
Ph. D. 1967 - "Spectroscopic Study of Color Centers and Eu^{2+} in LaCl_3 "	
J. Barry	Research Assistant (Summer)
L. Riseberg	Research Assistant
Ph. D. 1968 - "Multiphonon Orbit-Lattice Relaxation of Excited States of Rare Earth Ions in Crystals"	
R. Meltzer	Research Associate
J. Wright	Research Assistant

Publications

Fluorescence Decay of Rare-Earth Ions in Crystals by G. E. Barasch and G. H. Dieke. J. Chem. Phys. 43, 988 (1965).

Electron Paramagnetic Resonance and Optical Zeeman Spectra of Type II $\text{CaF}_2:\text{Er}^{3+}$ by C. W. Rector, B. C. Pandey and H. W. Moos. J. Chem. Phys. 45, 171 (1966).

Multiphonon Relaxation in $\text{LaCl}_3;\text{Nd}^{3+}$ by W. D. Partlow and H. W. Moos. Phys. Rev. 157, 252 (1967).

Electron Paramagnetic Resonance and Spectroscopic Study of $\text{LaCl}_3:\text{Eu}^{2+}$ and Associated Color Centers by B. F. Kim and H. W. Moos. Phys. Rev. 161, 869 (1967).

Vibronic Transitions of Hexagonal Rare-Earth Trichlorides. I. Pr^{3+} and Nd^{3+} in NdCl_3 by Elisha Cohen and H. W. Moos. Phys. Rev. 161, 258 (1967).

Vibronic Transitions of Hexagonal Rare-Earth Trichlorides. II. Pr^{3+} in LaCl_3 , PrCl_3 , and GdCl_3 by Elisha Cohen and H. W. Moos. Phys. Rev. 161, 268 (1967).

Effective Density of Phonon States for NdCl_3 from Vibronic Spectra and Applications to Ion-Lattice Interactions by E. Cohen, L. A. Riseberg and H. W. Moos. Phys. Rev. 175, 521 (1968).

Crystal Spectroscopy at The Johns Hopkins University by H. M. Crosswhite and H. W. Moos, in Optical Properties of Ions in Crystals, Interscience Publishers, New York (1967).

Multiphonon Orbit-Lattice Relaxation in LaBr_3 , LaCl_3 , and LaF_3 by L. A. Riseberg and H. W. Moos. Phys. Rev. Letters 19, 1423 (1967).

New Satellite Structure of Nd^{3+} Ions in Rare-Earth Trichlorides by G. A. Prinz and E. Cohen. Phys. Rev. 165, 335 (1968).

Multiphonon Orbit-Lattice Relaxation of Excited States of Rare-Earth Ions in Crystals by L. A. Riseberg and H. W. Moos. Phys. Rev. 174, 429 (1968).

Multiphonon Relaxation in Laser Materials and Applications to the Design of Quantum Electronic Devices by L. A. Riseberg, H. W. Moos and W. D. Partlow. IEEE J. Quantum Electronics QE-4, 609 (1968).

Spectroscopic Determination of the Magnon Density of States of a Ferromagnetic Rare Earth Salt, GdCl_3 by R. S. Meltzer, E. Cohen and H. W. Moos. Phys. Rev. Letters 21, 1690 (1968).

Spectroscopic Observation of Magnetic Ordering in DyPO_4 Using Line Intensity Measurements by J. C. Wright and H. W. Moos. To be published in Physics Letters A.

Spectroscopic Relaxation Processes of Rare-Earth Ions in Crystals by H. W. Moos. To be presented at International Conference on Luminescence, August, 1969, and to be published in Proceedings of Conference.

Summary of Program

The program was initiated in March 1963 by the late Dr. G. H. Dieke. Upon his death in August 1965, Dr. H. W. Moos became the project director. The primary goal of the program was to broaden existing knowledge of rare earth ions in crystals since there were a number of important unstudied problems, some of them crucial for application of the rare earth ions to electronic devices. The energy levels of the ions in simple crystals were relatively well known. However, little was known about the interaction of the ion with the phonons in the crystal, the transfer of excitation from one energy level to another, the effects of charge compensation when ions of one valence are doped into a crystal site of a different valence, the interaction of the ions with each other, etc. Quite a bit of progress has been made in areas of this type during the tenure of this grant as is indicated by the attached list of publications.

The early fluorescence lifetime studies have been extended. We now know that rare earth ions relax from one level to another with the emission of several phonons. Further, the relaxation rate depends critically on the number of phonons emitted and it is now possible to predict whether a level will relax or fluoresce. The attached paper reviews the status of work of this type, most of which has been done here. As the paper indicates, there are still a number of important problems which require study.

The vibronic side bands which appear near the main spectral lines have been used to study the phonons in the crystals and extract an effective density of phonon states.

The spectra of trivalent rare earths in CaF_2 have been studied with high resolution optical Zeeman spectroscopy and electron paramagnetic resonance and the type of charge compensation deduced. A similar study has also been made on Eu^{2+} in LaCl_3 .

More recently our attention has been drawn to using high resolution spectroscopic techniques to study the magnetic properties of the rare earth salts. The magnon density of states in a rare earth salt (GdCl_3) was obtained spectroscopically for the first time. Using spectroscopic techniques on DyPO_4 we have been able to obtain the magnetic phase diagram.

In conclusion, the funds supplied by this grant have been used to extend our knowledge of the rare earth ions in crystals. In addition to the scientific importance of the results outlined above, they will be useful in applied work. The field of optical electronics is broad, ranging from TV phosphors to computer memories. It is expected that the work supported by this program will provide perspective in the utilization of rare earth ions in these devices.

Spectroscopic Relaxation Processes of Rare Earth Ions
in Crystals

by H. Warren Moos
Department of Physics, The Johns Hopkins University

Presented at the
International Conference on Luminescence
August, 1969

Abstract

Relaxation processes between stark groups in the $(4f)^n$ energy levels of rare earth salts are discussed. The low temperature spontaneous relaxation rates are exponential in the energy gap to the next lowest stark group. The rates are determined primarily by the order of the process and the strength of the orbit lattice interaction. With increasing temperature stimulated emission of phonons by thermal phonons increases the rate. The presence of molecular groups and $4f^{n-1} 5d$ bands can cause quite different rates and temperature dependences. Excitation migration to special sites is suggested as a primary mechanism in ion pair relaxation.

I. Introduction

The 4f orbits of rare earth ions are so deeply buried within the electronic shell that the energy levels of the $(4f)^n$ configuration are only slightly perturbed when the ion is placed within a crystal. Generally the spin orbit splitting of the levels is $\sim 10^3 \text{ cm}^{-1}$ while the crystalline stark splitting of a level of given J is $\sim 100 \cdot \text{cm}^{-1}$. As a result of the relatively weak interaction with the environment, the picture of an isolated ion slightly perturbed by the surrounding crystal has been extremely fruitful. Further, it has been possible to use the rare earth ions as probes to observe solid state phenomena such as phonons and magnetic interactions. Spectroscopic relaxation is closely related to these latter studies.

It is well known that the rare earths fluoresce more or less efficiently depending on the nature of the host. At low concentrations, energy can be transferred to the vibration of molecular groups such as waters of hydration. In simple ionic crystals with relatively low maximum phonon energies of a few hundred wave numbers, characteristic energy gaps to the next stark group are found.¹ Stark groups with energy gaps greater than this value fluoresce strongly, groups with lesser gaps, weakly. This is due to energy transfer to the lattice vibrations, the critical gap representing the point at which the transfer rate is exceeded by the radiative fluorescence rate.

At higher concentrations, energy is transferred to other rare earth ions. Thus, if the differences in energy levels are sufficiently

close, a rare earth ion can relax from some excited state, C to a lower state A, raising another ion from its ground state Z to an excited state X. ²

The purpose of this paper is to review recent progress and some of the problems in this field of spectroscopic relaxation. Although we are able to give qualitative "hand waving" explanations for most of the observed relaxation phenomena, a scientific theory is only satisfactory (and useful) to the extent it can make predictive (hopefully quantitative) statements about new situations; i. e., if we dope n% of ion X into lattice Y will level A fluoresce? Our ability to do this is severely limited at the present time. Only by a careful understanding of the fundamental mechanisms will we come to the point where these very important predictive statements can be made. Therefore, elementary processes will be emphasized here. We will not attempt to survey the literature except as it helps to demonstrate a point. A note of apology is due to other workers. Because of familiarity rather than relative importance, the Johns Hopkins work has been emphasized.

Except for Sm^{2+} , the discussion is limited to trivalent rare earth ions. It is expected that many of the ideas discussed will be applicable to other types of ions.

II. Multiphonon relaxation

At low concentrations, the fluorescence decay rate of a level

is the sum of the radiative decay and multiphonon relaxation rates. The multiphonon relaxation rate can be obtained from the fluorescence decay rates by determining either the quantum efficiency for relaxation to the next lowest level or the quantum efficiency for all fluorescence from the upper level. The former was used for most of the data reported here.^{3,4} Measurements of the second kind are quite difficult but Weber⁵ has had remarkable success in computing the total radiative decay rates using measured oscillator strengths from the ground state.

It is found for the lower (distant from the 5d levels) $(4f)^n$ levels of the trivalent rare earths in simple ionic hosts that the multiphonon relaxation rates depend, except for a few exceptional cases, only weakly on the detailed nature of the electronic levels and vary exponentially in a given host with the energy gap to the next lowest level. It is also found that these relaxation rates increase sharply at elevated temperatures. The basic problem is first an experimental one, to measure these rates and determine their variation with gap and temperature, and secondly to explain the reasons for the variation. We discuss first the theoretical background⁴, then the present experimental results and finally a number of exceptions due to the proximity of the 5d bands and the presence of molecular groups.

To a good approximation the ion can be treated as isolated in a sea of phonons. Designating the electronic wave function by ψ and the i^{th} phonon normal mode with occupation number n_i by $|n_i\rangle$,

the system goes from an initial state

$$\chi_a = \psi_a \prod_i |n_i\rangle \quad (1a)$$

to a final state

$$\chi_b = \psi_b |n_j+1\rangle |n_k+1\rangle \cdots \prod_i |n_i\rangle. \quad (1b)$$

The number of phonon states with nearly the same frequency is high and it is very improbable that an occupation number would change by more than one.

Following the procedure which has been so successful in electron paramagnetic resonance, the interaction of the rare earth ion with the phonons is assumed to be due to modulation of the crystalline field by the motion of the ions⁶ causing a breakdown of the Born Oppenheimer approximation. This orbit lattice interaction is a function of the electronic and ionic coordinates, the latter being a function of the normal mode coordinates, Q_i . The interaction potential can be expanded in a Taylor series in Q_i :

$$V_{OL} = V_c + \sum_i V_i Q_i + \sum_{i,j} \frac{1}{2} V_{ij} Q_i Q_j + \cdots \quad (2)$$

where V_c is the static crystalline field and the higher expansion coefficients are derivatives of the crystalline field evaluated at the equilibrium position; $V_i = \partial V_c / \partial Q_i$, $V_{ij} = \partial^2 V_c / \partial Q_i \partial Q_j$, etc. Thus any given term in the sum is a product of a function of the electron coordinates times the phonon coordinates.

There are several ways in which a Hamiltonian of this type

can connect states χ_a and χ_b which differ in several phonon occupation numbers. A given Q_i in the interaction term can only connect states which differ by one in the same occupation number n_i . However, $V_{ij} Q_i Q_j$ can connect states differing by one in n_i and one in n_j , etc. Thus multiple phonon emission with simultaneous relaxation to a lower electronic state can occur by a coupling between χ_a and χ_b caused by a high order term in the expansion of the orbit lattice energy. Secondly χ_a and χ_b can be coupled by the first order term $\sum_i V_i Q_i$ via virtual intermediate states in high order perturbation theory. Finally it is possible that the $|n_i\rangle$ are not true harmonic states and the first order term could lead to direct coupling. In any case it is clear that it is an extremely complex phenomenon. Consider a transition between electronic states ψ_a and ψ_b with the emission of p phonons. The transition rate due to the first two processes is

$$\begin{aligned}
 W^{(p)} = & (2\pi/\hbar) \sum_{i \dots j m_1 \dots m_{p-1}} | \langle n_i+1 | Q_i | n_i \rangle |^2 \dots | \langle n_j+1 | Q_j | n_j \rangle |^2 \\
 & \times \frac{ | \langle \psi_b | V_i | \psi_{m_{p-1}} \rangle |^2 \dots | \langle \psi_{m_1} | V_j | \psi_a \rangle |^2 }{ (E_{m_{p-1}} + \hbar\omega_j + \dots + \hbar\omega_{i-1} - E_a)^2 \dots (E_{m_1} + \hbar\omega_j - E_a)^2 } \times g(\omega_i) \dots g(\omega_j) \delta(E_b + (\hbar\omega_i + \dots + \hbar\omega_j) - E_a) \\
 & + \frac{2\pi}{\hbar} \sum_{i \dots j} (1/n!)^2 | \langle \psi_b | V_{i \dots j} | \psi_a \rangle |^2 | \langle n_i+1 | Q_i | n_i \rangle |^2 \dots | \langle n_j+1 | Q_j | n_j \rangle |^2 \\
 & \times g(\omega_i) \dots g(\omega_j) \delta(E_b + \hbar\omega_i + \dots + \hbar\omega_j - E_a)
 \end{aligned} \tag{3}$$

where $|\psi_{m_k}\rangle$ is an intermediate virtual state and $g(\omega_k)$ is the frequency density of phonon states. The electronic states are assumed to be very narrow and the δ functions maintain energy conservation. Cross terms between the two processes have not been included. Most of the multiplying terms in this expression are poorly known if at all. Kiel⁷ had some success in obtaining rough order of magnitude estimates by using the first order term with high order perturbation theory but because of the extreme complexity, any attempt at systematic computation of the rates appears extremely difficult. However, it turns out that it is just this complexity which permits a very simple phenomenological theory to be used. As a first approximation, one expects that the lowest order process dominates so that only a given $W^{(p)}$ contributes. There are still an extremely large number of ways in which p phonons can be emitted; the sums over phonon modes and intermediate states are essentially a statistical average of products of matrix elements. As a result, one would expect that except for rigorous selection rules, the numerical value of $W^{(p)}$ should not depend markedly on the character of the electronic states ψ_a and ψ_b . Spin is usually not a good quantum number due to the large spin orbit coupling in the rare earths, most of the phonons are of low symmetry, and these rigorous selection rules are probably few. At the present time the only experimentally observed rule is the slowness of relaxation from $J = 1$ to $J = 0$ states. This is due to the vanishing of matrix elements connecting pure $(4f)^n$, $J = 1$ and 0 states.

In the phenomenological approach we postulate that the ratio of the p^{th} and $p-1^{\text{th}}$ processes will be given by some coupling constant

$$\epsilon = \frac{W(p)}{W(p-1)} \ll 1 \quad (4)$$

characteristic of the host crystal but not the rare earth electronic state. ϵ varies only slowly with p . For a given lattice at low temperature the spontaneous relaxation rate varies approximately as

$$W(p) = A \epsilon^p \quad (5)$$

ΔE , the energy gap, is related to p by

$$p = \frac{\Delta E}{\hbar \omega} \quad (6)$$

where ω is the frequency of the dominant phonons. Generally the lowest order process dominates and $\omega \sim \omega_{\text{max}}$. Hence, we expect

$$W = B e^{\alpha \Delta E} \quad (7)$$

where B and α are characteristic of a given host. The closeness of a given rate to the average behavior given by Eq. (7) is a measure of the extent to which the sums of Eq. (3) are a statistical average. Evidently the averages are surprisingly good. The rates are usually within a factor of two or three of Eq. (7). Fig. 1 shows the results for a number of levels in LaCl_3 , LaBr_3 and LaF_3 .⁸

The results are even more striking when plotted against the order of the process. The vibronic side bands which appear near the electronic transition can be used for many crystals to obtain the effective phonon frequency distribution function.⁹ In particular, the maximum phonon frequency can be usually obtained from the extent of the peaks. The relaxation rates can then be plotted against the normalized energy gap $\Delta E/\hbar\omega_{\max} \sim$ the order p . The surprising result is that the relaxation rates for a number of hosts all crowd together on this plot. Fig. 2 shows this effect for LaCl_3 , LaBr_3 and LaF_3 . LaCl_3 and LaBr_3 are very similar crystals with identical symmetries and almost identical crystal field splittings of the energy levels. However, the respective maximum phonon energies are 260 cm^{-1} and 175 cm^{-1} . When corrected for this difference in the phonon energies, the data fall on top of each other. LaF_3 has a different symmetry with crystal field splittings typically twice as large as those of LaCl_3 and phonons out to 350 cm^{-1} . When corrected to normalized energy gaps, the LaF_3 data are close but not identical. If the strength of the orbit lattice interaction increases as the static crystal field, one would expect for a given order the LaF_3 transition rate would be higher and secondly the downward slope would be less. This is what is observed. Fig. 3 shows normalized curves for five crystals. The only surprising result is Y_2O_3 . It has a much larger crystal field splitting, 1.5-2 times that of LaF_3 yet it seems to have a relatively weak orbit lattice interaction. It may be that this is due to the relative covalency of the crystal and further work is required

on crystals of this type. In spite of this, it is now clear that it is possible in many cases to make rough estimates of multiphonon relaxation rates. The phonon spectrum can be obtained from the vibronics and a few measured rates will determine the curve.

It appears, then, that there is a way of systematizing the experimental relaxation rates for simple ionic crystals in terms of the order of the process and a coupling constant ϵ . The important theoretical problem is the computation of ϵ rather than individual rates. Of course the above statements are only tentative until a much larger amount of data has been gathered and one of the important experimental problems is to determine the limitations of this phenomenological approach.

We have really been working backwards from theory to experiment when, of course, things really went the other way. So it is appropriate that we take up the temperature dependence last. It was a study of this which gave the first strong experimental proof that the relaxation process was a multiple emission of phonons with the lowest order process dominating.^{3, 10} From the presence of the term $|\langle n_i + 1 | Q_i | n_i \rangle|^2$ in Eq. (3) it is obvious that a process which leads to emission of a phonon of type i will be proportional to $\bar{n}_i + 1$ where the average occupation number

$$\bar{n}_i = [\exp \hbar \omega / k T - 1]^{-1} \quad (8)$$

is determined by the ambient temperature. The $\bar{n}_i$ contributes to

the stimulated or induced part of the relaxation rate. When several phonons are emitted, the energies and hence occupation numbers are approximately the same and

$$W^{(p)}(T) = W_o^{(p)} \left(1 + \bar{n} \left(\frac{\hbar\omega}{kT}\right)\right)^p \quad (9)$$

where $W_o^{(p)}$ is the rate at low temperatures and the average phonon energy $\hbar\omega = \Delta E/p$. There is some justification for the statement that the phonons have similar energies in the observation that the effective phonon frequency distribution function for LaCl_3 contains most of its intensity between 150 and 260 cm^{-1} . Also, the exponential dependence of equation 8 implies that a product of the type $(\bar{n}_i+1)(\bar{n}_j+1)(\bar{n}_k+1)\dots$ will have a maxima at $\omega_i = \omega_j = \omega_k \dots$. Fig. 4 shows Eq. (9) computed for several values of p for a 1100 cm^{-1} gap. It is obvious that the order of the process can easily be determined from the temperature dependence. Data of this type cannot be fit with an activation energy, $e^{-\Delta E/kT}$ dependence.

Fig. 5 shows relaxation from the $E(^6F_{3/2})$ to $D(^6F_{5/2})$ levels of $\text{LaBr}_3:\text{D}_y^{3+}$ fitted for temperature dependent multiphonon relaxation. Sometimes the higher levels of a stark group can relax only by a higher order process and ions in these levels essentially do not contribute to the relaxation process. This can actually lead to a decrease in the relaxation rate at slightly elevated temperatures as these levels are populated. Fig. 6 shows the temperature dependence of the multiphonon transition rate from $F(^5F_3)$ to $E(^5F_4, ^5S_2)$

of $\text{LaF}_3:\text{Ho}^{3+}$. There is a definite drop in the rate going from 4° to 80° K.

A large number of levels have been studied and fitted with dependences of the type of Eq. 9. This is remarkable evidence that the relaxation process is caused by the emission of p phonons. p is usually the lowest order possible.

At this point, one might think that the problem of multiphonon relaxation is a closed one. However, there are complications which must be considered. We consider here the presence of molecular groups and the proximity of the 5d bands.

The vibration frequencies of molecular groups are narrow with little dispersion with k so that only limited frequencies are available for relaxation. Secondly, although the group as a unit may be the primary source of the crystalline field splitting of the rare earth, the vibration of the molecular group may have a lesser interaction than the lattice vibrations which involve the rare earth. CaWO_4 , which is a relatively efficient fluorescer, is an example of this. The lattice modes involving the motion of the group as a whole go out to $\sim 200 \text{ cm}^{-1}$, but there are also vibrations of the tungstate complex out to $\sim 900 \text{ cm}^{-1}$. A comparison of three levels is given in Table I. There are one to two orders of magnitude difference between these rates and what one would predict from Fig. 3. It is clear then that the molecular group vibration in CaWO_4 must interact very weakly with the rare earth.

Waters of hydration provide high frequency vibrations and hydrated crystals are generally noted as poor fluorescers. Heber et al.¹¹⁻¹³

have studied fluorescence in compounds such as Eu ethylsulfate $\cdot 9 \text{ H}_2\text{O}$, $\text{Eu}(\text{BrO}_3)_3 \cdot 9 \text{ H}_2\text{O}$, $\text{EuCl}_3 \cdot 6 \text{ H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6 \text{ H}_2\text{O}$, $\text{Eu}_2(\text{SO}_4)_3 \cdot 8 \text{ H}_2\text{O}$ and a number of similar compounds. Multiphonon relaxation rates for $\text{Eu}^{3+}: {}^5\text{D}_0$ ($\sim 2 \times 10^3$) and $\text{Tb}^{3+}: {}^5\text{D}_4$ ($\sim 7 \times 10^3$) vary by less than a factor of 2 over these compounds, indicating the constancy of the interaction with the H_2O molecule. The ${}^5\text{D}_1$ to ${}^5\text{D}_0$ relaxation of Eu^{3+} was also measured and was relatively slow ($\sim 10^4$) for a gap of only 1760 cm^{-1} , indicating the $J = 1 \rightarrow J = 0$ selection rule.

Only a little bit of work has been done on the rare earth $(4f)^n$ levels in close proximity to the $4f^{n-1} 5d$ bands. Partlow et al.¹⁴ have studied the ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ relaxation rate in two sites in $\text{LaCl}_3:\text{Sm}^{2+}$. The basic result is that 1) the ${}^5\text{D}_1 \rightarrow {}^5\text{D}_0$ relaxation is quite rapid, especially when one considers the forbiddenness of $J = 1 \rightarrow J = 0$ and 2) the temperature dependence of the rate cannot be fit by a multiphonon process (Partlow et al. found that a 20-40 phonon process would be required to fit the data) but by an activation energy; i. e., $W = A e^{-\Delta E/kT}$. For the two sites studied, $\Delta E = 650 \text{ cm}^{-1}$ and 1300 cm^{-1} .

In $\text{LaCl}_3:\text{Sm}^{2+}$ most of the ${}^5\text{D}_1$ population relaxes to the ${}^5\text{D}_0$ and it appears that a model of the type shown in Fig. 7 may be the basic mechanism. The Sm^{2+} ion is thermally excited upwards to a $4f^{n-1} 5d$ level, relaxes rapidly downward and finally goes from the bottom of the level to the ${}^5\text{D}_0$ level. The transitions from the $4f^n$ ground state to the $4f^{n-1} 5d$ bands commence about 1500 cm^{-1} above ${}^5\text{D}_1$ so that transitions to the relevant $4f^{n-1} 5d$ levels in Fig. 7 are

inhibited by Franck-Condon or other selection rules. If this mechanism is correct, it would mean that the orbit lattice interaction between the $(4f)^n$ and $(4f)^{n-1} 5d$ states is quite strong, since the excitation rate is very large, $>10^8$ but requires the absorption of several phonons to reach the $4f^{n-1} 5d$ level.

Further evidence is found in the decrease in the lifetime of the 5D_0 level at room temperature. Alam et al.¹⁵ report similar behavior for the 5D_0 level of $SrF_2:Sm^{2+}$. They fit the temperature dependence of the lifetime with an activation energy of 515 cm^{-1} . It is quite possible that in addition to divalent ions, the upper $(4f)^n$ levels of trivalent rare earths may exhibit similar effects due to proximity to the $4f^{n-1} 5d$ levels. Of course, the above is quite tentative and much more work is required on this type of relaxation mechanism, but it appears that the proximity of the $4f^{n-1} 5d$ bands alters the nature of the relaxation process in a very striking way.

III. Ion pair relaxation

The relaxation of an ion from an excited level to a lower one exciting a nearby ion as shown in Fig. 8 is a well-established relaxation mechanism in rare earth salts. The phenomena are somewhat more complicated than indicated since the transitions are between groups of stark levels and in addition the absorption or emission of phonons may be required to conserve energy. The process is important in potential quantum electronic materials and this has spurred interest.

At the present time it is generally possible to explain the results post facto in terms of Fig. 8. However, we have very little understanding in terms of computing (or even measuring) the relaxation rates for a given set of levels. There is not even a phenomenological approach such as Eq. 5 which has been so useful in collecting and correlating multiphon relaxation data. One might say that our predictive capacity was extremely poor. As a measure of the experimental problems consider the pair process for like ions shown in Fig. 8b. In this simple system, there is no way of distinguishing between the processes shown by the solid and dashed lines.

The theory of the transfer mechanism has been given by Dexter.¹⁶ An initially excited ion A^* undergoes a transition $A^* \rightarrow A$ which is described by a normalized line shape function $g_A(E)$. The energy yielded in this transition is taken up by a transition $B \rightarrow B^*$ in a nearby ion. If V is the interaction Hamiltonian which produces the transfer of energy, the probability for transfer per unit time is:

$$P = \frac{2\pi}{h} | \langle A B^* | V | A^* B \rangle |^2 \int g_A(E) g_B(E) dE \quad (10)$$

V is expanded in terms of multipoles in the near zone limit ($R \ll \lambda$) and the rate estimated from the highest order non vanishing terms. Order of magnitude estimates of the electric dipole interaction indicate that it is small. It is not clear which of the higher order

interactions dominate because of widely different wavelength and distance dependences. Exchange is also important. As an indication of the problem, Table 2, taken from Birgeneau¹⁷, lists experimental (electron paramagnetic resonance) and calculated matrix elements for the various interactions between 1st and 6th near neighbor pairs of Ce³⁺ and Nd³⁺ in LaCl₃. The matrix elements are of comparable size and which one dominates depends on the ion and energy levels under consideration. Exchange is especially important since the J selection rule is $(\Delta J) \leq 7$ permitting almost any transition of interest and very few selection rules except conservation of energy are to be expected.

The experimental situation is also somewhat cloudy. Concentration studies have been used. A mean effective distance, R between ions is assumed to vary as the inverse cube root of the concentration. Since a given order multipole varies as R^{-n} , n can be deduced from the dependence of the fluorescence efficiency on the concentration.¹⁸

Quantum efficiency and relative fluorescence intensity measurements are extremely powerful. Fig. 9 shows the energy levels of LaCl₃:Ho³⁺. By exciting C and monitoring the radiation from E, C and Y, it has been possible to demonstrate that the dominant relaxation mechanism of E is ion pair relaxation to C exciting a nearby ion to Y or the equivalent (see Fig. 8b); i. e., the number of photons coming from C and Y is twice the number

of photons absorbed but not radiated from E.¹⁹ The pair relaxation rate in 2.0% $\text{LaCl}_3:\text{Ho}^{3+}$ is $\sim 1 \times 10^3$ varying linearly with concentration.

At first the above would seem to be a nice tidy problem. However, consider the following results.²⁰ When J is excited part of the population relaxes. This process requires the emission of a $\sim 150 \text{ cm}^{-1}$ phonon in order to conserve energy. The vibronic side bands are down by about 10^{-3} and from Eq. 10 one would expect an appropriate decrease in the $J \rightarrow E$ rate. However, measurements indicate that it is of the same order as $E \rightarrow C$. In addition, part of the J population relaxes directly to C without going to E. There is no possible pair process for this and the only mechanism left is a three ion process in which $J \rightarrow C$ while simultaneously exciting two adjacent ions from $Z \rightarrow Y$. The appearance of these two processes which are expected to be weak, present an important problem.

Not too much is known about the randomness of the site distribution. A more important factor may be the role of exciton migration which increases the importance of special sites. Exciton migration is relatively well established as a source of quenching in concentrated crystals²¹ and even such exotic processes as exciton-exciton annihilation leading to the creation of a higher energy exciton have been demonstrated.^{21,22} However, we really know very little about this process. For instance, the role of homogenous vs. inhomogenous broadening of energy levels in exciton migration

has not been examined. It may well be that a better understanding of processes such as exciton migration may be required before we can understand ion pair interactions. In any case, the problem of pair relaxation is certainly a wide open one and there is much to be learned before we can make even order of magnitude estimates.

Acknowledgements

The author wishes to acknowledge the many contributions made by W. B. Gandrud, W. D. Partlow, J. F. Porter, Jr., and L. A. Riseberg to much of the work reviewed here. The work at Johns Hopkins has been supported by NASA and the U. S. Army Research Office-Durham.

Table I
Multiphonon Relaxation Rates in CaWO_4

<u>Level</u>	<u>Energy Gap (cm^{-1})</u>	<u>Rate</u>	<u>Estimated No. of Phonons</u>
Er K($^2\text{H}_{9/2}$)	1800	$>10^6$	2 molecular
Ho E($^5\text{F}_4$, $^5\text{S}_2$)	2600	$\sim 10^4$	3 molecular
Er E($^4\text{S}_{3/2}$)	2900	$\sim 10^4$	3 molecular + 1 lattice

Table II

Matrix Elements of Magnetic Dipole-Dipole,
Exchange, and Electric Quadrupole-Quadrupole
Interaction Between the Ground States of Ce^{3+}
and Nd^{3+} in LaCl_3 ; in Units of cm^{-1} (from Ref. 17).

	<u>Ce^{3+} in LaCl_3</u>		<u>Nd^{3+} in LaCl_3</u>	
	1st nn	6th nn	1st nn	6th nn
Magnetic Dipole	-0.042	-0.005	-0.042	-0.005
Exchange	0.10	---	~ 0.25	~ 0.002
Electric Quadrupole	2.40	0.072	0.002	0.00006
Separation ($\text{\AA}$)	4.375	8.750	4.375	8.750

References

1. G. H. Dieke in Paramagnetic Resonance, ed. by W. Low, Academic Press (1963), Vol. 1, p. 237.
2. F. Varsanyi and G. H. Dieke, Phys. Rev. Letters, 7 (1961) 442.
3. W. D. Partlow and H. W. Moos, Phys. Rev. 157 (1967) 252.
4. L. A. Riseberg and H. W. Moos, Phys. Rev. 174 (1968) 429, and references therein.
5. See, for instance, M. J. Weber, Phys. Rev. 171 (1968) 283.
6. R. Orbach, Proc. Roy. Soc. (London) A264 (1961) 458.
7. A. Kiel in Quantum Electronics, ed. by P. Grivet and N. Bloembergen (Columbia Univ. Press, 1964), Vol. 1, p. 765; also Ph.D. dissertation, The Johns Hopkins University, 1962 (unpublished).
8. L. A. Riseberg and H. W. Moos, Phys. Rev. Letters 19 (1967) 1423.
9. E. Cohen, L. A. Riseberg and H. W. Moos, Phys. Rev. 175 (1968) 521.
10. J. R. Chamberlain, D. H. Paxman and J. L. Page, Proc. Phys. Soc. 89 (1966) 143.
11. J. Heber, Phys. Kondens. Materie, 6 (1967) 381.
12. J. Heber, K. H. Hellwege, D. Mangelsdorf and W. Zieg, Phys. Kondens. Materie, 5 (1966) 89.
13. J. Heber and K. H. Hellwege in Optical Properties of Ions in Crystals, ed. by H. M. Crosswhite and H. W. Moos, Interscience (1967) 457.

References (Cont'd)

14. W. D. Partlow, H. W. Moos, J. C. Wright and E. H. Carlson
to be published.
15. A. S. M. M. Alam and B. DiBartolo, J. Chem. Phys. 47 (1967)
3790.
16. D. L. Dexter, J. Chem. Phys. 21 (1953) 836.
17. R. J. Birgeneau, Appl. Phys. Letters 13 (1968) 193.
18. See, for instance, L. G. Van Uitert, J. Electrochemical Soc.
114 (1967) 1048.
19. J. F. Porter, Jr. and H. W. Moos, Phys. Rev. 152 (1966) 300.
20. J. F. Porter, Jr., Bul. Amer. Phys. Soc. 13 (1968) 102,
and private communication.
21. W. B. Gandrud and H. W. Moos, J. Chem. Phys. 49 (1968) 2170.
22. W. D. Partlow, Phys. Rev. Letters 21 (1968) 90.

Figure Captions

- Fig. 1 Spontaneous multiphonon transition rates of trivalent rare earth ion energy levels in LaCl_3 , LaBr_3 and LaF_3 vs. the gap to the next lowest group. The empirical state designations are given by Dieke (Ref. 1).
- Fig. 2 The data of the previous figure as a function of the normalized energy gap.
- Fig. 3 Spontaneous multiphonon transition rate as a function of normalized energy gap for five crystals. The gaps have been divided by 360 cm^{-1} for SrF_2 and 550 cm^{-1} for Y_2O_3 .
- Fig. 4 Eq. 9 as a function of temperature for a 1100 cm^{-1} gap and for 4, 5, and 6 phonon processes.
- Fig. 5 Temperature dependence of multiphonon transition rate from the E level of $\text{LaBr}_3:\text{Dy}^{3+}$ with a gap of 775 cm^{-1} . The theoretical fit is for five 155 cm^{-1} phonons using Eq. 9. The error bars indicate absolute probable error whereas the relative error between points is much smaller.
- Fig. 6 Temperature dependence of the multiphonon transition rate from the F level of $\text{LaF}_3:\text{Ho}^{3+}$. The theoretical curve is

for emission of six 300 cm^{-1} phonons with thermal depopulation to a single non-decaying level 150 cm^{-1} above the lowest and five non-decaying levels 500 cm^{-1} above the lowest. The relative error between points is much smaller than the absolute probable error bars shown.

- Fig. 7 Schematic representation of proposed relaxation mechanism for ${}^5D_1 \rightarrow {}^5D_0$ in $\text{LaCl}_3:\text{Sm}^{2+}$.
- Fig. 8 Schematic representation of pair processes. (a) Unlike ions in which 3 relaxes to 2, exciting $1'$ to $2'$ in a nearby ion. (b) Like ions in which the processes represented by the solid and dashed lines cannot be distinguished.
- Fig. 9 Partial energy level diagram of $\text{LaCl}_3:\text{Ho}^{3+}$. Pendants identify levels which fluoresce in $\text{LaCl}_3:\text{Ho}^{3+}$.

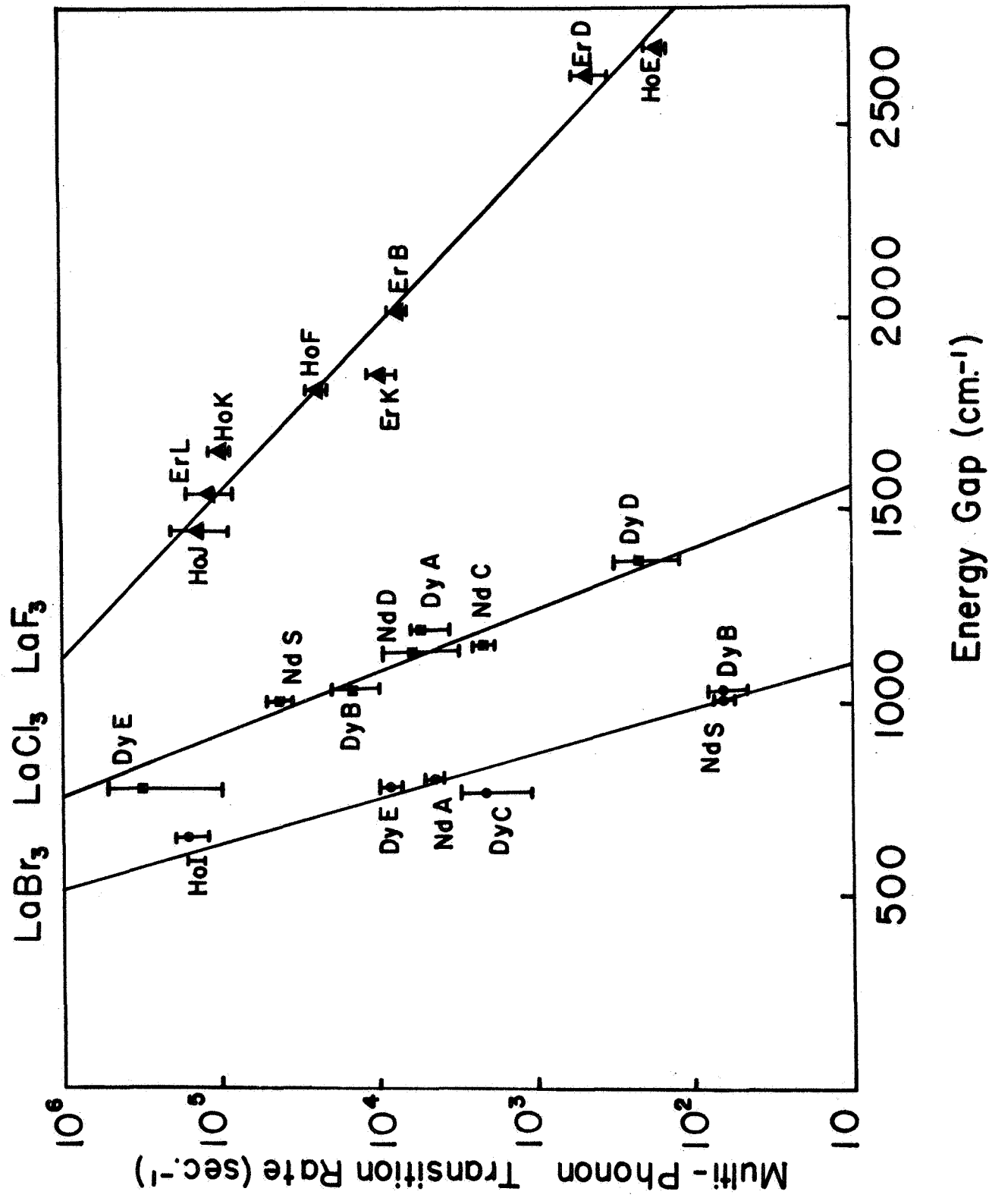


Fig. 1

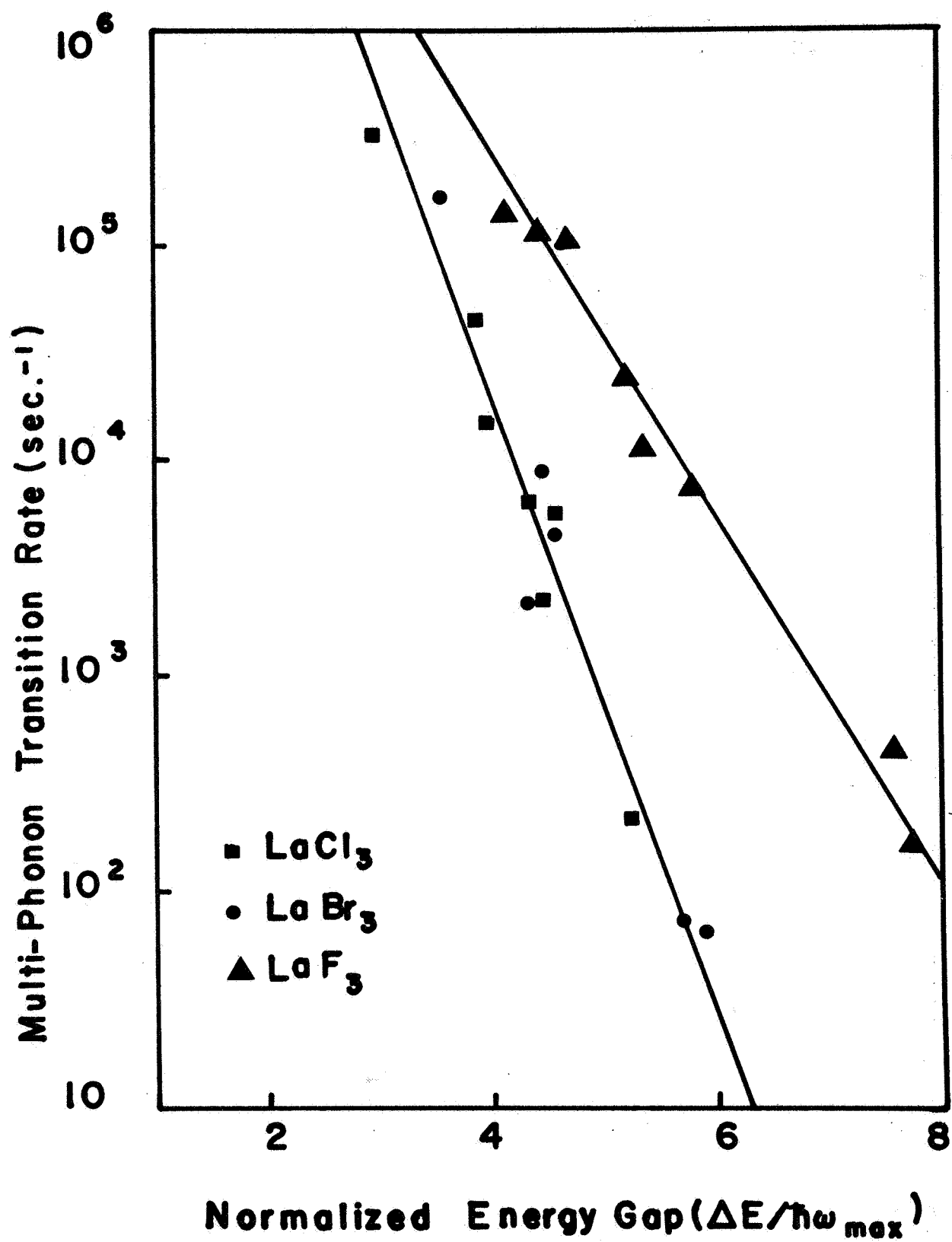


Fig. 2

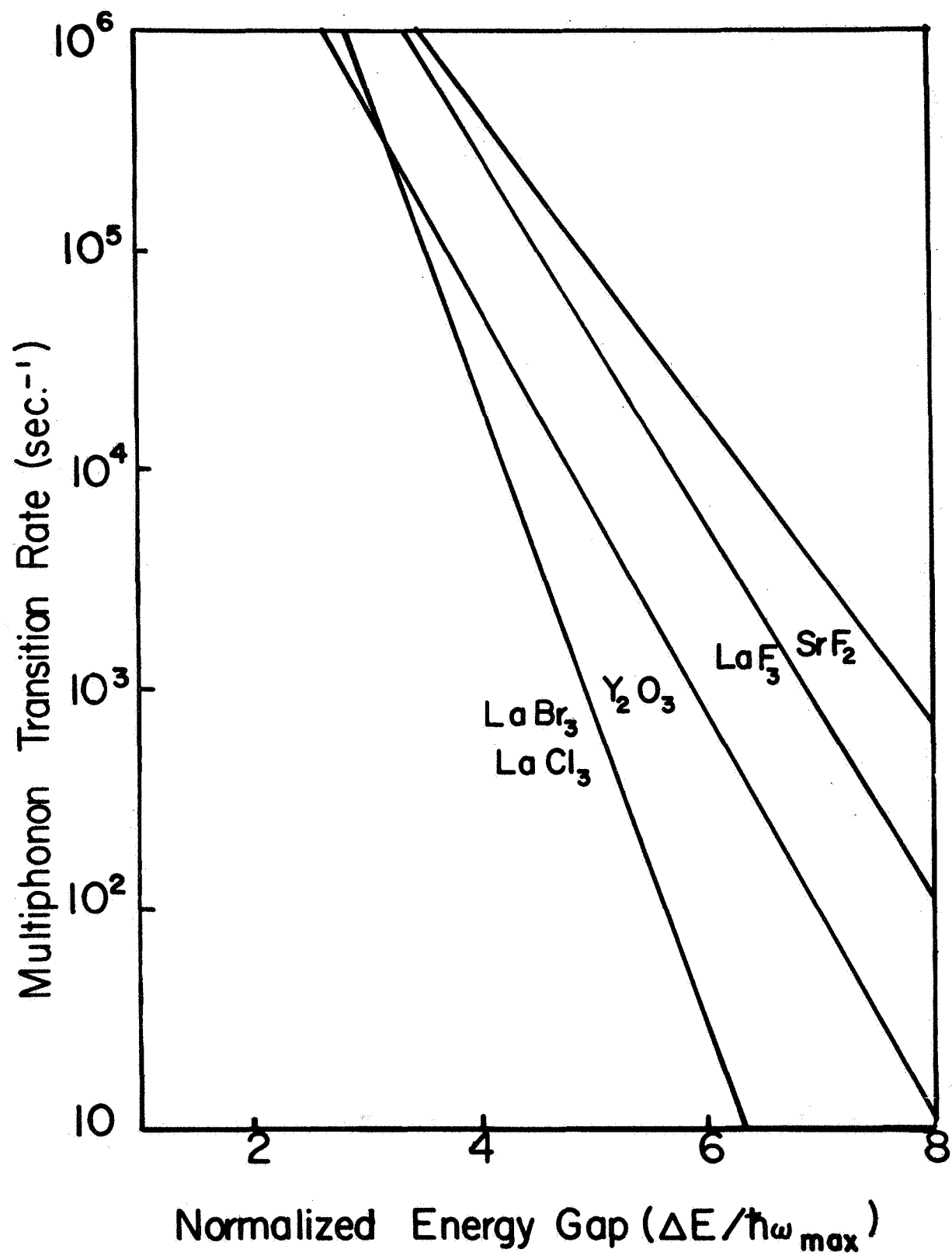


Fig. 3

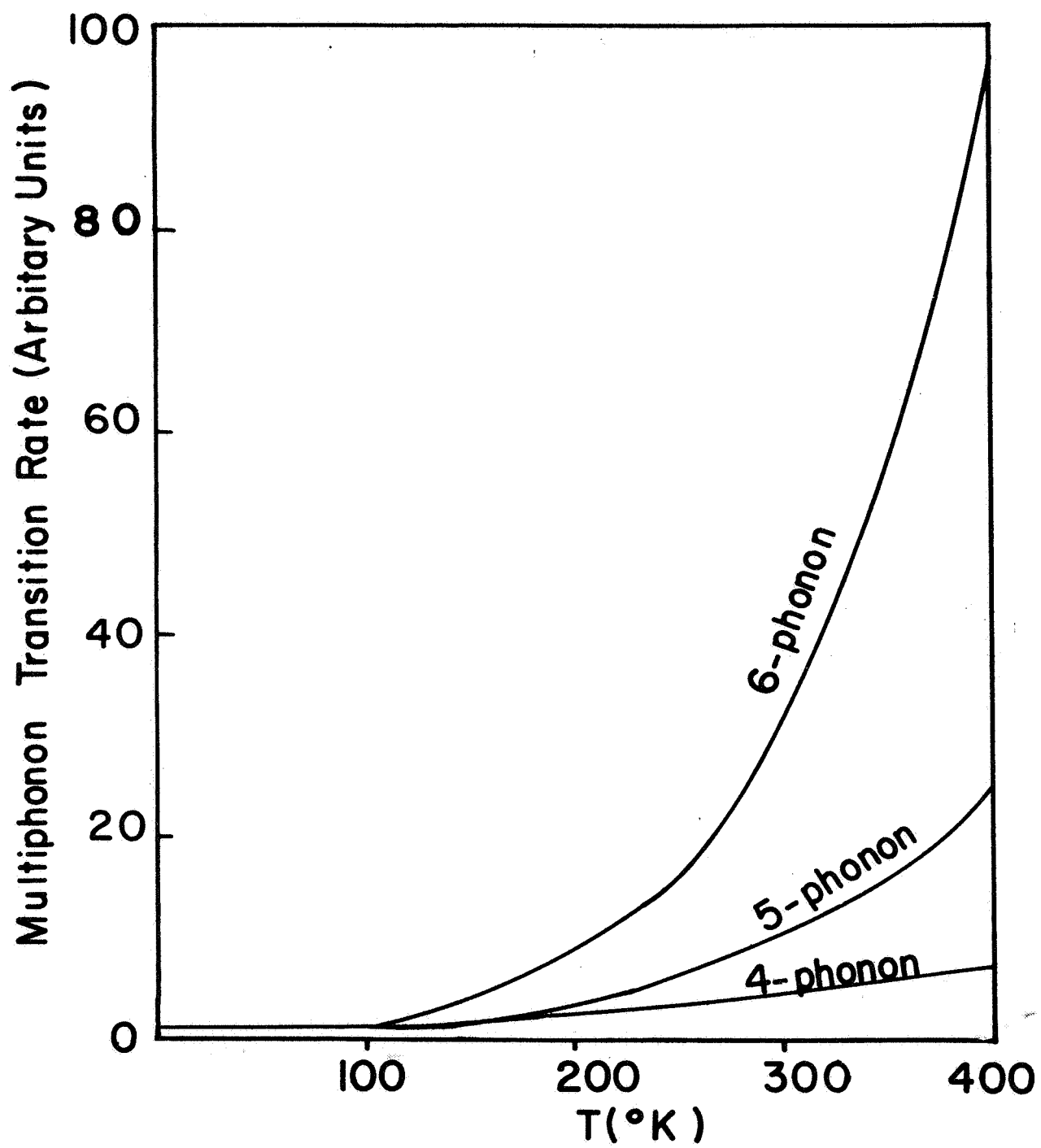


Fig. 4

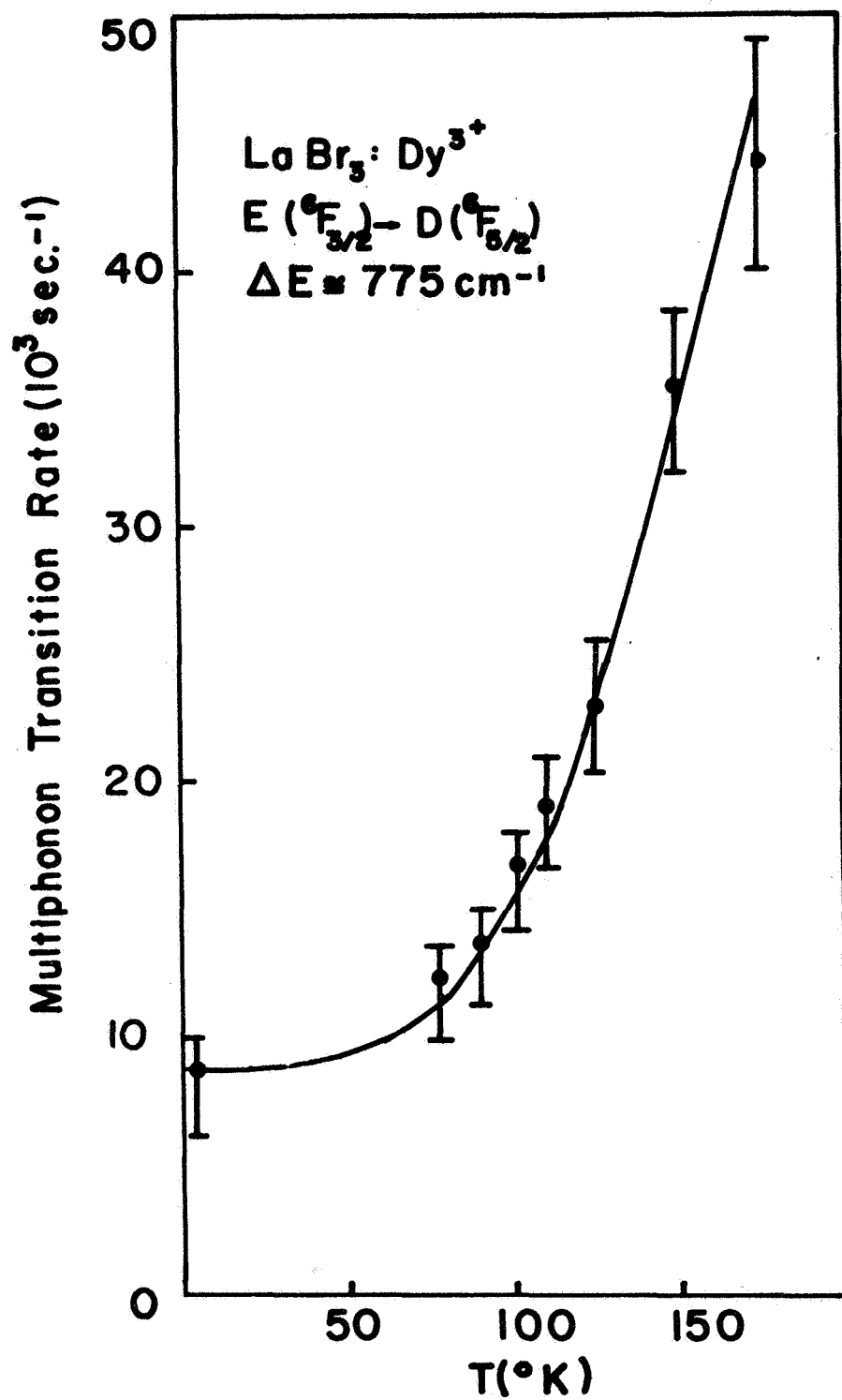


Fig. 5

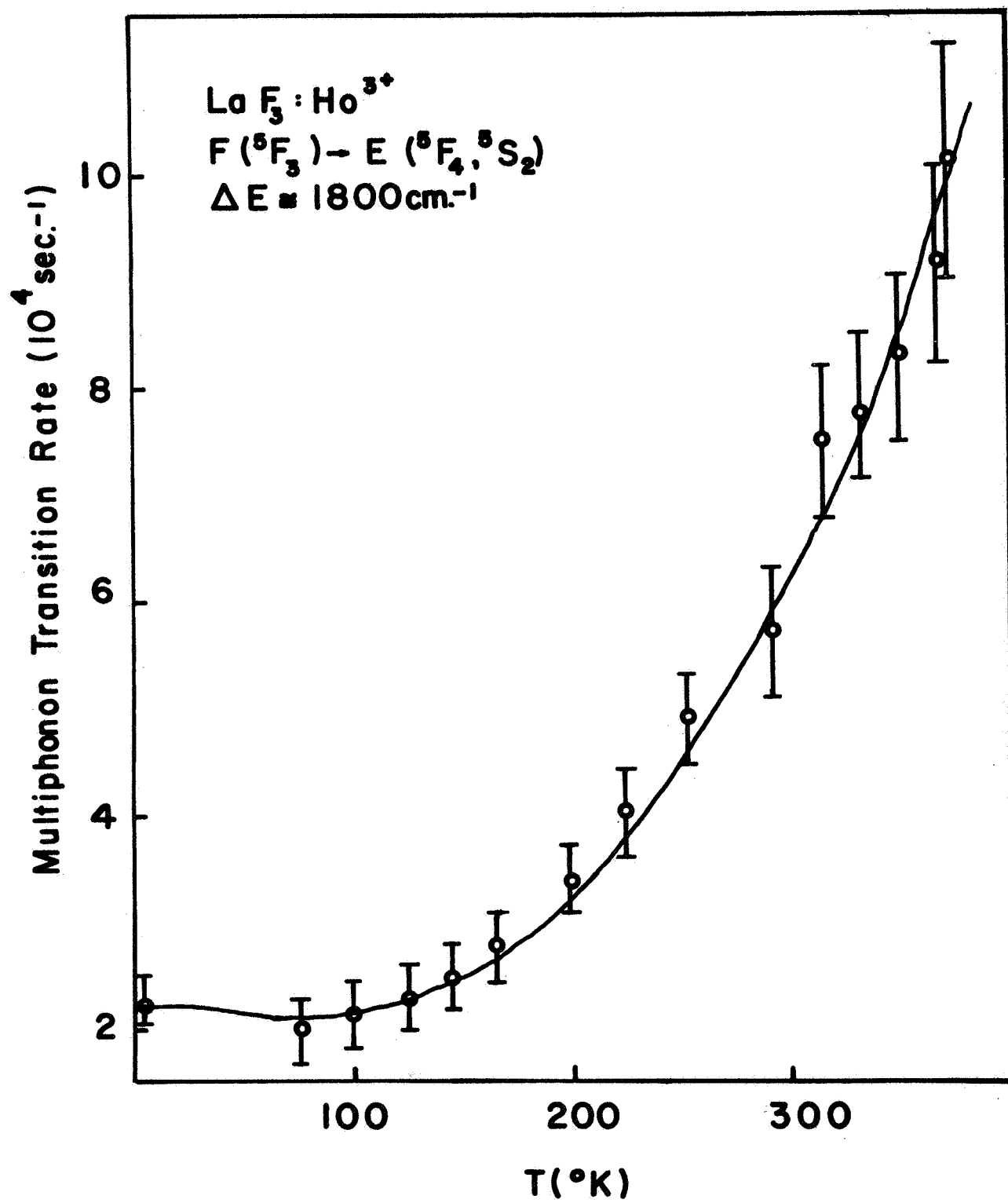


Fig. 6

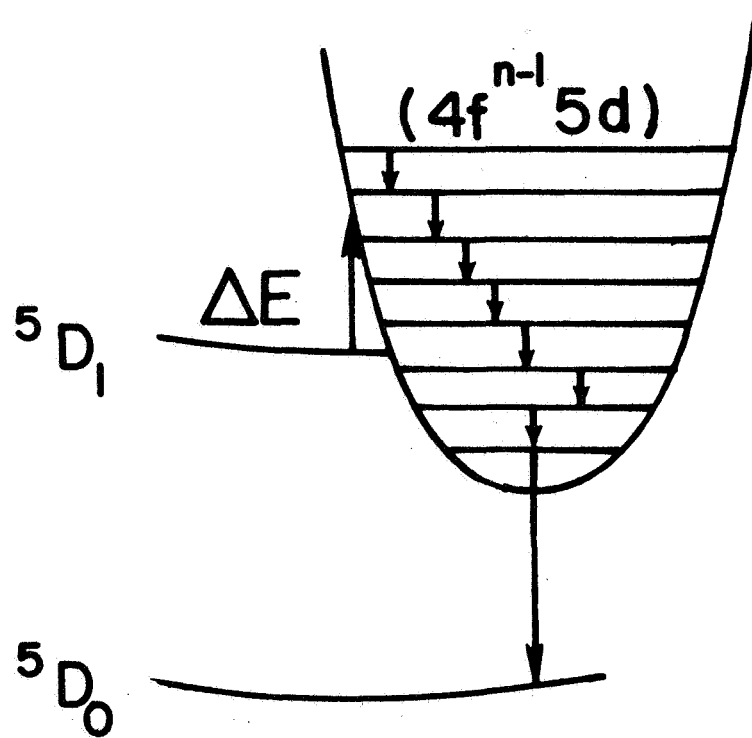
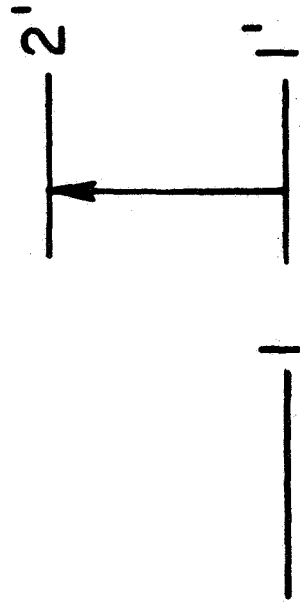
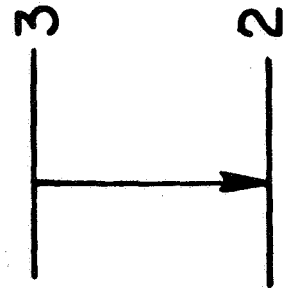
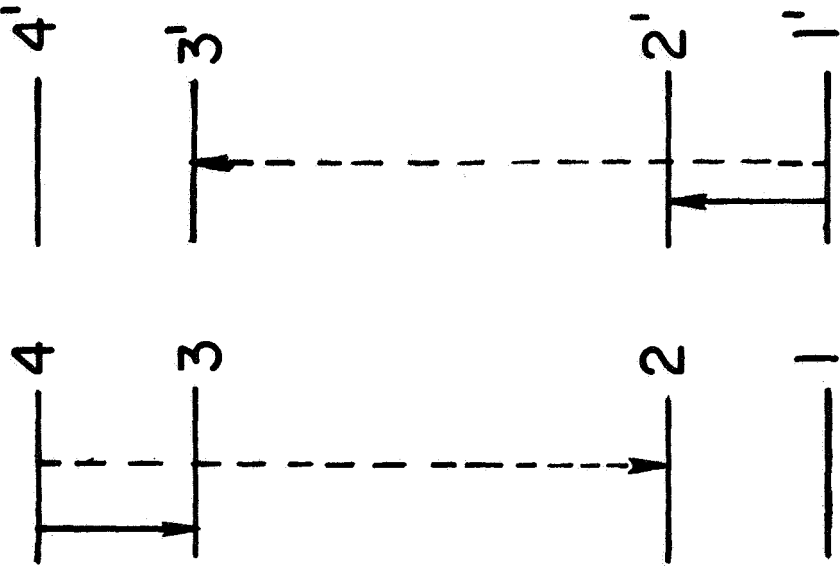


Fig. 7



(a)



(b)