TABLE I. Values of the various parameters used in the phonon-conductivity calculations of $CdCl_2$ and $FeCl_2$.

$FeCl_2$	$A=1.127\times10^4$ $H_{44}=3.36\times10^4\ \mathrm{sec}^{-1}$	$B=10^{-5}\ \mathrm{sec}^{-1}\,{}^\circ\mathrm{K}^{-4}$ $H_{31}=1.7375\times10^4\ \mathrm{sec}^{-1}$	$E=2.874\times10^{-7}\ \mathrm{sec}^{-1}\,{}^\circ\mathrm{K}^{-5}$ $\Theta_D=162\,{}^\circ\mathrm{K}$
$CdCl_2$	$A=1.127\times10^4$	$B=10^{-5}\ \mathrm{sec}^{-1}\,{}^\circ\mathrm{K}^{-4}$	$E=2.874\times10^{-6}\ \mathrm{sec}^{-1}\,{}^\circ\mathrm{K}^{-5}$

basically ruled out due to the fact that the thermal-conductivity variation within this region is found to be proportional to T^3. Another possibility would have been the inclusion of critical-fluctuation scattering with the direct (resonant) phonon absorption and emission within crystal and exchange-field-split energy levels of the Fe^{2+} ion. However, this would not improve the agreement within the first maximum region since in this region the scattering rate due to critical fluctuations dominates that due to the direct processes. Hence, the resultant effect would be to get a still lower value for the thermal conductivity.

The case of nonmagnetic $CdCl_2$ is a bit simpler in that only the three types of phonon scattering mechanisms, viz., boundary, point-defect, and the umklapp, are operative. Callaway's integral then takes the form

$$\kappa(T)=AT^3\int_0^{\Theta_D/T}\frac{x^4e^x(e^x-1)^{-2}dx}{1+Bx^4T^4+Ex^2T^5}\ .$$

The various parameters used are given in Table I. We find that we have successfully accounted (Fig. 2) for the results of $CdCl_2$ with the exception that there remain slight deviations around the temperature of 17 °K. This deviation may be attributed to the presence of some impurities in the sample which cause the extra phonon scattering near this temperature.

---

[1] G. Laurence, Phys. Letters 34A, 308 (1971).

[2] K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 29, 801 (1963).

[3] H. Stern, J. Phys. Chem. Solids 26, 153 (1965).

[4] D. Huber, Solid State Commun. 6, 685 (1968).

[5] R. Alben, J. Phys. Soc. Japan 26, 261 (1969).

PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Drift Mobilities of Holes and Electrons in Naphthalene Single Crystals*

W. Mey and A. M. Hermann
Department of Physics, Tulane University, New Orleans, Louisiana 70118

(Received 16 June 1972)

The drift mobilities of holes and electrons in very pure single crystals of naphthalene were experimentally determined by measurement of transit times of transient space-charge-limited currents. The room-temperature values are in general agreement with published data except for holes in the $\vec{c}\,'$ direction where a larger value of 0.99 $\mathrm{cm}^2/\mathrm{V\,sec}$ was measured. In the temperature range 220–300 °K, the mobilities of holes and electrons were found to vary as $T^{-2.1}$ and $T^{-0.9}$, respectively, in the $\vec{c}\,'$ direction, while the mobility of holes was found to vary as $T^{-1.0}$ for the $\vec{a}$ crystal direction and as $T^{-0.8}$ for the $\vec{b}$ crystal direction. While these results are consistent with band calculations based on the tight-binding approximation, the mobilities of electrons in the $\vec{a}$ and $\vec{b}$ crystal directions were found to be essentially independent of temperature, and hence cannot be accounted for by band theory. The experimental results are compared with predictions of the band and hopping models, and it appears that the transport mechanism is intermediate between these two modes of transport.

INTRODUCTION

The charge carrier transport properties of organic molecular crystals have been reported by many investigators.[1-4] Mobilities in these crystals, anthracene being a prototype, are generally of the order of 1 $\mathrm{cm}^2/\mathrm{V\,sec}$ and hence cannot be used to determine if either a band or a hopping model is applicable in describing their transport properties.[5] The electronic transport properties of anthracene have been studied by Kepler[1] and LeBlanc.[2] In general it was found that drift mobilities of both holes and electrons varied with temperature according to T^{-n} where $1<n<2$. However for the electrons in the $\vec{c}\,'$ direction the mobility was found to increase slightly with increasing temperature. Band calculations by LeBlanc[6] succeeded in explaining the observed anisotropy of mobilities as well as their temperature dependence except for c′ electrons. Subsequent tight-binding calculations by Katz *et al.*,[7] Silbey *et al.*,[8] Thaxton *et al.*,[9] and Glaeser and Berry,[10] resulted in changing the predicted anisotropy of mobilities but still could not account for the anomalous temperature dependence of the $\vec{c}'$ electron mobility.

Glaeser and Berry[10] have made calculations based on the hopping model. Their calculations agree with the observed anisotropy of mobilities in anthracene but the temperature dependency is not discussed. Holstein[11] formulated a hopping model which describes the transport of charge carriers interacting with molecular vibrations. However, when applied to anthracene, it could not account for the temperature dependencies of mobility for values of parameters consistent with other experimental and theoretical data.[12] Munn and Siebrand[12–14] have extended the Holstein model to include quadratic electron-phonon interactions. Their model, when applied to anthracene, successfully accounted for the observed temperature dependence of mobility in all directions.

The aforementioned models have also been applied to naphthalene whose crystal structure is identical to anthracene aside from the lattice spacing. It is therefore of interest to determine experimentally mobilities in naphthalene and compare the results to those predicted by these models. In the work reported here, measurements of the temperature dependence of mobilities of both holes and electrons in naphthalene single crystals are presented. In general mobilities decrease with increasing temperature except for electrons in the $\vec{a}$ and $\vec{b}$ crystal direction where the mobility is essentially independent of temperature. The results are compared with band calculations based on the tight-binding approximation and with various hopping models.

EXPERIMENTAL PROCEDURE

The naphthalene crystals were obtained from I. Zschokke-Granacher at the Institut Fur Angewandte Physik Der Universitat Basel. High-purity naphthalene was zone refined with 50 passes in a Pyrex tube. Material from the center of the zone-refined samples was placed in a smaller cylindrical Pyrex tube which was then evacuated. The single crystals were grown from the melt in a Bridgman furnace. The purification and growing process was carried out in the dark. Crystal directions were determined with the aid of a Bausch and Lomb polarizing microscope and the optical techniques discussed by Nakada.[15] The oriented sections were cut with an S. S. White Airdent Unit and an optical finish was obtained by polishing them on tissue wetted with benzene.

The experimental technique used was that developed by Kepler[1] and LeBlanc.[2] The light source consisted of a xenon lamp (Xenon Corporation -S-130B flashtube and Model 465-A Micropulser) with an output of 5 J and a rise time of approximately $\frac{1}{2}$ μsec. The sample was sandwiched between two electrodes. The front electrode was quartz, coated with a tin oxide layer, while the back electrode was silver conductive paste, painted on the rear surface of the sample. The temperature of the sample was varied by blowing cold dry nitrogen gas into the sample cell. A copper-constantan thermocouple imbedded in a "dummy" crystal (anthracene) was used to monitor the temperature. The drift mobilities were experimentally determined by measurement of the transit time of transient space-charge-limited currents. Evidence of space-charge-limited currents was the square-law dependence of the initial current density j_0 on the applied voltage, and 20% increase of the transit time upon significant reduction of the light intensity.[16] The mobility for each data point reported here was obtained from the slope of a plot of the inverse of the transit time (transit time having been corrected for space-charge effects) versus applied voltage. At least three different voltages were used to determine these curves and in all cases they passed through the origin indicating field-independent mobilities and the absence of trapped space charge. In order to eliminate the effects of trapped space charge the method described by Nakada and Ishihara[17] was used. After each measurement the front and rear electrodes were shorted and several light pulses were incident upon the crystal to neutralize the space charge.

RESULTS

The temperature dependence of the mobilities was measured in the range 200-300 °K in three crystal directions. These measurements were made on two samples taken from different boules. In Fig. 1 the variation of the electron and hole mobilities with temperature is shown for the $\vec{c}'$ direction. The room-temperature mobility was found to be 0.68 cm^2/V sec for electrons and 0.99 cm^2/V sec for holes. This hole mobility is a factor of two higher than the value reported by Silver *et al.*[18] and Spielberg *et al.*,[19] but is in agreement with the tight-binding calculations of Katz *et al.*[7] which predict the mobility of holes in the $\vec{c}'$ direction to be intermediate between those values in the $\vec{a}$ and $\vec{b}$ directions. The negative temperature coefficient for the $\vec{c}'$ electron mobility is to be contrasted with positive coefficient found previously for anthracene.[1,17] From a log-log plot with a least-squares fit, it was found that the mobility of holes varied at $T^{-2.1}$ and electrons as $T^{-0.9}$.

Figure 2 shows the variation of the electron and

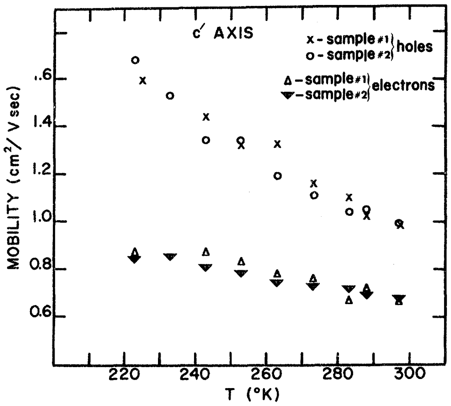

FIG. 1. Mobility vs temperature for electrons and holes in the $\vec{c}'$ direction.

hole mobilities with temperature for the $\vec{a}$ direction. The room-temperature mobilities were found to be 0.88 cm²/V sec for holes and 0.51 cm²/V sec for electrons in general agreement with previously published results.[18,19] From a log-log plot with a least-squares fit, the mobility of holes was found to vary as $T^{-1.0}$ and the electron mobility was found to be essentially independent of temperature.

Figure 3 shows the variation of mobility with temperature for the $\vec{b}$ direction. Room-temperature mobilities were found to be 1.41 and 0.63 cm²/V sec for holes and electrons, respectively, in general agreement with the results of Silver *et al.*[18] and Spielberg *et al.*[19] A log-log plot with a least-squares fit revealed that the hole mobility varied as $T^{-0.8}$ while the electron mobility was essentially independent of temperature. Table I shows a summary of the experimental results of this work.

DISCUSSION

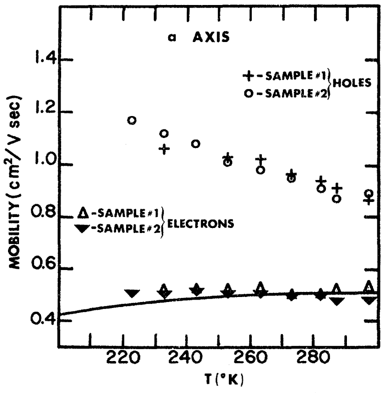

FIG. 2. Mobility vs temperature for electrons and holes in the $\vec{a}$ direction.

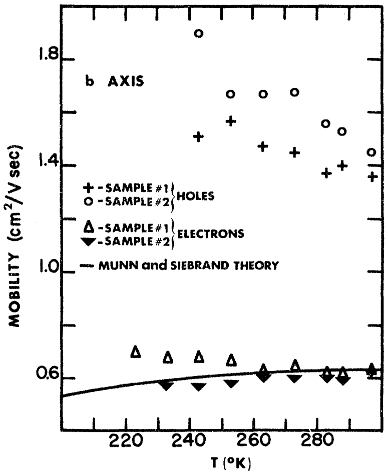

FIG. 3. Mobility vs temperature for electrons and holes in the $\vec{b}$ direction. The solid curve is the Munn–Siebrand prediction (see discussion).

There are two basic models which have been proposed for describing the electrical transport properties of organic molecular crystals, the band model (delocalized representation), and the hopping model (localized representation). We shall first discuss the predictions of the band model.

Band calculations for naphthalene based on the tight-binding approximation have been made by Katz *et al.*,[7] Silbey *et al.*,[8] Thaxton *et al.*,[9] and Glaeser and Berry.[10] In the tight-binding calculation the constant-mean-free-path or constant-relaxation-time approximation is used and only mobility ratios, not their absolute values, are predicted. Table II shows the mobility ratios for naphthalene calculated by Katz *et al.* For hole mobilities there is good agreement with our experimental results. The bandwidth calculated by Katz *et al.* for holes in the $\vec{a}$ direction is about a factor of 10 smaller than for the $\vec{c}'$ direction, but the measured mobilities are about the same. Since an increase in bandwidth results in an increase in mobility,[5] it appears that the bandwidth calculated for holes in the $\vec{a}$ direction is too narrow. Siebrand reached the same conclusion from theoretical consideration of electron-phonon coupling in naphthalene.[20]

For electron mobilities, the agreement between the band theory and our results are not as good as for holes. The bandwidth calculated by Katz *et al.* for electrons in the $\vec{c}'$ direction is smaller than in

TABLE I. Summary of experimental results.

Crystal direction	Mobility (room temp.) (cm²/V sec)		Temp. exponent n ($\mu \propto T^{-n}$)	
	Holes	Electrons	Holes	Electrons
$\vec{c}'$	0.99	0.68	2.1	0.9
$\vec{a}$	0.88	0.51	1.0	0.1
$\vec{b}$	1.41	0.63	0.8	0.0

TABLE II. Ratios of drift mobilities in naphthalene.

	Hole mobilities			Electron mobilities		
	$\frac{\mu_{aa}}{\mu_{bb}}$	$\frac{\mu_{bb}}{\mu_{c'c'}}$	$\frac{\mu_{aa}}{\mu_{c'c'}}$	$\frac{\mu_{aa}}{\mu_{bb}}$	$\frac{\mu_{bb}}{\mu_{c'c'}}$	$\frac{\mu_{aa}}{\mu_{c'c'}}$
Band model (Katz *et al.*)	0.14	5.6	0.76	1.6	25	39
Hopping model (Glaeser *et al.*)	0.36	1.1	0.38	1	2.2	2.2
Present work	0.62	1.42	0.89	0.81	0.93	0.75

both the $\vec{a}$ and $\vec{b}$ directions. But the measured mobility for electrons in the $\vec{c}\,'$ direction is slightly higher than in the $\vec{a}$ or $\vec{b}$ directions. Hence, from our data, it appears that the bandwidth calculated for electrons in the $\vec{c}\,'$ direction is too narrow.

It is difficult to discuss the temperature dependence of the drift mobility from the tight-binding calculations of Katz *et al.*[7] In these calculations coherent transport is assumed and the electron-phonon interaction is expected to result in a mobility which decreases with increasing temperatures. This interaction is introduced through a parameter (constant free time or constant free path) which varies with temperature, but its dependence is not discussed, in general, quantitatively. A quantitative treatment of electron-phonon interactions in organic molecular crystals was given by Glarum.[5] Glarum found that when the bandwidth is much smaller than kT the mobility varies at T^{-2}, but when the bandwidth is much larger than kT, the mobility varies as $T^{-1.5}$. So in general when considering only single-acoustical-phonon scattering processes in the band model, the mobility varies as T^{-n} where $n < 2$. Glarum points out, however, that the exact value of n is a sensitive function of bandwidth and anisotropy. Friedman[21] has also formulated a theory of electron-phonon scattering based on the tight-binding approximation. His theory, which is similar to that of Glarum, predicts that mobility should vary as T^{-2}. A possible lower limit in n might be unity, for example, as would be the case for scattering by nonionized impurities.[22] Summarizing the above discussion, we find that the band model predicts that mobilities should vary at T^{-n} where $1 < n < 2$. Hence it appears that this coherent-transport (band) model can account for the experimentally observed temperature dependencies in all directions in naphthalene except for electrons in the $\vec{a}$ and $\vec{b}$ direction. The electron mobilities in these directions are essentially temperature independent, and hence cannot be accounted for by band theory.

Another mechanism for describing transport is the hopping model. In this model the charge carrier is quasilocalized at a particular molecular site and occasionally makes phonon-assisted transitions to neighboring sites. These phonon-assisted transitions can be caused by hopping over the intermolecular barrier or by tunneling through the barrier. The process of hopping over the intermolecular barrier is a thermally activated one and therefore cannot account for our results.[10] Glaeser and Berry[10] have made calculations for naphthalene assuming that hopping occurs by phonon-assisted tunneling through the intermolecular barrier. Table II shows their predicted mobility ratios for naphthalene. As can be seen, the agreement is quite good. In contrast with the band model, the hopping model predicts the absolute magnitude of the mobilities (to well within an order of magnitude) as well as the relative anisotropy. Glaeser and Berry do not discuss the temperature dependence of mobility associated with their model and hence a comparison with our experimental results cannot be made. They do, however, indicate that their model cannot be rejected on the basis of experimentally determined temperature dependence of drift mobility because the tunneling mechanism is not a thermally activated process.

Another tunneling model is that of Keller and Rast[23] which involves a one-dimensional square-well potential which is perturbed by the lattice vibrations. Tredgold[24] has shown, however, that this model results in a mobility that is an increasing function of temperature (although not of an activated form) and hence cannot account for our results.

Holstein[11] formulated a hopping model which describes the transport of charge carriers interacting with molecular vibrations. However, when applied to anthracene, it could not account for the temperature dependencies of mobility for values of parameters consistent with other experimental and theoretical data.[12] Munn and Siebrand believe that this failure is apparently due to the neglect of quadratic electron-phonon coupling terms. Munn and Siebrand[12–14] have made some recent theoretical hopping and coherent transport calculations which they applied to anthracene. Their model, which extended the theory of Holstein to include quadratic electron-phonon interactions, successfully accounted for the positive temperature dependence of electron mobility in the $\vec{c}\,'$ direction. The parameters necessary to make a quantitative comparison of their model with our experimental results are not as well known as for anthracene. However, a qualitative comparison of our data with the predicted temperature-dependent mobility of the Munn-Siebrand model can be made. In order to compare our data to the predictions of the Munn–Siebrand theory, the following procedure was used. The mode of transport was assigned according to the observed temperature dependence of the mobility. A temperature-independent mobility or a mobility whose temperature coefficient is positive is assigned to either hopping in the slow-electron limit or the slow-phonon limit. An out-of-plane bending mode ($\hbar\omega_0$) was then chosen and the expression for mobility was normalized to our room-temperature value. (It should be noted that once $\hbar\omega_0$ is chosen, this fixes the temperature dependence of the expression for mobility and only its magnitude can change.) The average out-of-plane bending frequency ($\hbar\omega_0$) for naphthalene should be at least as low as anthracene but probably somewhat higher.[12] Initially $\hbar\omega_0$ was chosen to be 350 cm^{-1} (the same as for anthracene). With this parameter, we eliminate the slow-phonon mode since it does not give adequate account of our data at low temperature. The expression for mobility which gave the best fit to our experimental results for electrons in the $\vec{a}$ and $\vec{b}$ direction was for hopping in the two oscillator slow-electron limit, and is given by

$$\mu^{(2)}_{(\text{hopping electron})} = \frac{4\pi J^2 d^2}{\hbar B} \frac{e}{kT} \frac{\sigma(1+\sigma^2)}{(1+\sigma)^3},$$

where $\sigma = \exp(-\hbar\omega_0/kT)$, d is the molecular separation, B is the phonon bandwidth, and J is the transfer integral; the subscript (hopping electron) denotes hopping transport in the slow-electron limit, and the superscript (2) refers to the two oscillator model. Plots of this function normalized to our room-temperature values are shown in Figs. 2 and 3 for electron mobility in the $\vec{a}$ and $\vec{b}$ directions, respectively, and are seen to give reasonable agreement with this experiment. However, for the same value of $\hbar\omega_0$ the Munn and Siebrand model could not account for the remainder of our experiment results. Furthermore, $\hbar\omega_0$ for naphthalene is probably somewhat higher than for anthracene,[12] and values higher than 350 cm^{-1} give poorer agreement with the experiment.

The room-temperature Hall and drift mobilities in naphthalene were determined by Spielberg *et al.*,[19] from photo-Hall-effect measurements. They found that the tight-binding calculations of Katz *et al.*,[7] yielded results which gave an order of magnitude agreement with their experimentally determined Hall to drift mobility ratios, and also yielded the correct sign for both holes and electrons. From this they concluded that the band model is applicable for describing the electrical transport properties of naphthalene. However, from our results of the temperature dependence of drift mobilities, we conclude that the band model cannot account for the temperature-independent mobilities of electrons in the $\vec{a}$ and $\vec{b}$ directions observed in naphthalene. It appears that neither the band model based on the tight-binding approximation nor the hopping models discussed above can account for all of our results. Glarum[5] has pointed out that for these organic insulators the transport mechanism is probably between that of the band model and that of the hopping model. This appears to be the case for naphthalene.

Further evidence regarding the transport mechanism in naphthalene could be obtained from the temperature dependence of the Hall mobility as well as measurements of mobilities in deuterated naphthalene (the Munn–Siebrand theory predicts an isotope effect for drift mobilities in naphthalene). We are presently investigating the temperature dependence of drift mobilities in deuterated naphthalene which will give further information regarding the applicability of the Munn–Siebrand model to organic molecular crystals.

ACKNOWLEDGMENTS

The authors would like to thank Dr. C. J. Fritchie of Tulane University and Dr. L. Gary of Loyola University for their help with preparation and orientation of the samples.

---

*Work supported by NASA.

[1] R. G. Kepler, Phys. Rev. 119, 1226 (1960).

[2] O. H. LeBlanc, Jr., J. Chem. Phys. 33, 626 (1960); J. Chem. Phys. 37, 916 (1962).

[3] A. I. Korn, R. A. Arndt, and A. C. Damask, Phys. Rev. 186, 938 (1969).

[4] R. Raman and S. P. McGlynn, J. Chem. Phys. 40, 515 (1964).

[5] S. H. Glarum, J. Phys. Chem. Solids 24, 1577 (1963).

[6] O. H. LeBlanc, Jr., J. Chem. Phys. 35, 1275 (1961).

[7] J. L. Katz, J. Jortner, S. I. Choi, and S. A. Rice, J. Chem. Phys. 39, 1683 (1963).

[8] R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, J. Chem. Phys. 42, 733 (1965); J. Chem. Phys. 43, 2925 (1965).

[9] G. D. Thaxton, R. C. Jarnagin, and M. Silver, J. Phys. Chem. 66, 2461 (1962).

[10] R. M. Glaeser and R. S. Berry, J. Chem. Phys. 44, 3797 (1966).

[11] T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959); Ann. Phys. (N. Y.) 8, 343 (1959).

[12] R. W. Munn and W. Siebrand, J. Chem. Phys. 52, 6391 (1970).

[13] R. W. Munn and W. Siebrand, Chem. Phys. Letters 3, 655 (1969).

[14] R. W. Munn and W. Siebrand, J. Chem. Phys. 52, 47 (1970).

[15] I. Nakada, J. Phys. Soc. Japan 17, 113 (1962).

[16] A. Many and G. Rakavy, Phys. Rev. 126, 1980 (1962).

[17] I. Nakada and Y. Ishihara, J. Phys. Soc. Japan 19, 695 (1964).

[18] M. Silver, J. R. Rho, D. Olmess, and R. C. Jarnagin, J. Chem. Phys. 38, 3030 (1963).

[19] D. H. Spielberg, A. I. Korn, and A. C. Damask, Phys. Rev. 3, 2012 (1971).

[20] W. Siebrand, J. Chem. Phys. 41, 3574 (1964).

[21] L. Friedman, Phys. Rev. 140, A1649 (1965).

[22] F. Gutmann and L. E. Lyons, *Organic Semiconductors*

(Wiley, New York, 1967), pp. 256–259.

[23] R. A. Keller and H. E. Rast, J. Chem. Phys. 36, 2640 (1962).

[24] R. H. Tredgold, Phys. Soc. Proceedings 80, 807 (1962).

PHYSICAL REVIEW B VOLUME 7, NUMBER 4 15 FEBRUARY 1973

Energy Transfer between Antimony and Manganese in the Fluorophosphate Phosphors

Thomas F. Soules, Robert L. Bateman, Ralph A. Hewes, and Eric R. Kreidler
Lighting Research and Technical Services Operation, General Electric Company, Nela Park,
Cleveland, Ohio 44112

(Received 26 July 1972)

The kinetics of energy transfer from antimony sensitizer to manganese activator in fluorophosphate phosphors has been studied. The transfer mechanism is identified as an exchange interaction by a comparison of the manganese concentration dependence of experimental quantum yield and emission decay curves with theoretical calculations for dipole-dipole, dipole-quadrupole, and exchange mechanisms. The probability per unit time for the energy transfer by exchange is given by $P=KR^{16}e^{-2R/L}\sin^2\theta\cos^2\varphi$, where the empirical parameters are $K=48.7$ Å^{-16} μsec^{-1} and $L=0.55$ Å. The antimony emission decay curve is found to be exponential in the absence of manganese acceptors, with a lifetime of 7.65 ± 0.05 μsec. The subsequent manganese emission decay is found to fit the sum of two exponentials with the main component having a lifetime of 14.3 ± 0.5 msec and the minor component (which comprises only about 3% of the total manganese emission) having a lifetime of 1.9 ± 0.1 msec.

I. INTRODUCTION

There have been numerous experimental studies of resonant energy transfer between impurity ions in inorganic solids.[1–3] Energy transfer, for instance, is important in the operation of many solid-state lasers utilizing rare-earth and transition-metal ions in various host crystals.

Energy transfer also plays a central role in the halophosphate phosphors containing antimony and manganese impurity ions. These phosphors are the most important commercial phosphors. They are extensively used in fluorescent lamps. In the operation of the lamp, ultraviolet radiation from the mercury discharge is absorbed by the antimony impurity centers. Some of the absorbed quanta are reemitted in a band peaking near 480 nm. Energy is also transferred to the manganese impurity ions which emit in the yellow region of the spectrum. The intensity of the manganese emission band is dependent on the acceptor concentration and is adjusted to provide a suitable white light in the lamp. However, while these gross features of the operation of the phosphor have been known for some time,[4] no detailed study of the energy transfer process has been made. Such a study is of interest not only because of its importance in the operation of the halophosphate phosphors but also because it is a prototype for energy transfer between an S^2 sensitizer and a transition-metal activator.

We present an analysis of the kinetics of energy transfer in fluorophosphate phosphors. We have found that the observed energy transfer can only be plausibly explained by assuming a nonradiative energy transfer using an exchange mechanism of interaction. The characteristics of the energy transfer more closely resemble those involved in the quenching of triplet states in organic phosphors than they do energy transfer which is induced by dipole-dipole or multipolar mechanisms. Triplet-triplet energy transfer has been extensively studied in organic systems[5] since its discovery by Terenin and Ermoleav.[6,7] The importance of exchange interactions in energy transfer in inorganic systems has recently been emphasized by Birgeneau *et al.*[8,9]

We found the careful measurement of the decay of the antimony luminescence to be particularly useful in characterizing the mechanism of energy transfer. It enabled us to determine the parameters in the exchange mechanism and to easily distinguish the mechanism of energy transfer from dipole-dipole and multipolar mechanisms. This would have been difficult if we had used the usual method of simply measuring the quantum yield and an average or apparent lifetime.[1,2] Inokuti and Hirayama,[10] who developed a quantitative theory of energy transfer by the exchange mechanism, emphasized the importance of a careful measurement of the decay of the donor luminescence in attaining a full knowledge of energy transfer.

In order to identify the acceptor centers, we also measured the luminescence and decay properties of the emission band peaking near 575 nm in the fluorophosphate phosphors. From electron-spin-resonance studies,[11] it is known that manganese substitutionally replaces calcium ions at the Ca(I) sites