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The Triplet Excitons in the Anion Radical Salts of $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$

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The electron spin resonance (ESR) absorption and its variation with the temperature were measured with single crystals of the anion radical salts containing the mixed cations, $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$. The paramagnetic excited state of these salts is triplet in character, as was shown from the anisotropic zero-field splitting at low temperatures. The triplet state is not localized, but, rather, corresponds to the triplet exciton state. The exciton exchange frequency and its temperature dependence were determined by analyzing the line shapes of the ESR spectra. The exciton motion in the mixed crystal system was investigated in order to establish the character of the triplet excitons in ion radical salts.

Much attention has been paid to the solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) because of their prominent electronic properties.1–24) In particular, the anion radical salts of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$ and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$ have been found to possess non-singlet, excited crystal states lying very close to a singlet ground state.6) These excited states are triplet in character, as has been demonstrated by electron spin resonance (ESR) studies of the anisotropic zero-field splitting.1) The excited states of such a system are thought not to be localized, but, rather, to correspond to the exciton states; that is, the excitation may propagate as a quasi-particle (*i.e.*, a triplet exciton).4)

On the other hand, one can prepare anion radical salts containing the mixed cations represented by $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$.2) In the present paper, we found that these mixed crystals also show the ESR spectra charac-

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teristic of the triplet excitons. At various temperatures, the exchange frequencies due to triplet exciton motion were evaluated by analyzing the line shapes of the observed ESR spectra. In these mixed crystals, if the mixed cations are randomly arranged, the crystal lattice will no longer be periodic. At this time, the triplet exciton exchange and the exciton motion will be much affected in the field of the irregular crystal lattice. In this respect, it is interesting to compare the results of our study with those of the regular crystal lattice for $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\cdot-}$ or $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\cdot-}$.[4)]

Experimental

Materials. The preparation of TCNQ has been described by Acker and Hertler.[25)] It was purified by recrystallization from acetonitrile. The anion radical salts containing the mixed cations, $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\cdot-}$, $(0 \leq x \leq 1)$, were synthesized according to the method of Melby *et al.*[2)] Six salts with the compositions of x=0.00, 0.20, 0.40, 0.60, 0.80, and 1.00 were prepared. They were taken from the same batches as those previously used for the differential scanning calorimeter (DSC) measurements and the electrical conductivity measurements.[20,22,23)]

Measurements. The ESR spectra of the single crystals (5 mm × 5 mm × 1 mm) in the temperature range from 112 K to 333 K were measured by means of a JES-ME X-band spectrometer. The steady magnetic field was modulated at 100 KHz, with a modulation amplitude of 0.32 gauss. The temperature of the specimen was controlled to within ±1 K by means of the temperature equipment.

Results

The ESR spectra of the triplet excitons in the anion radical salts of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\cdot-}$, $(x=0.00)$, and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\cdot-}$, $(x=1.00)$, have been described by Jones and Chesnut.[4)] Therefore, let us examine the mixed crystals below. As an example, the salt of $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\cdot-}$, $(x=0.80)$, will be investigated in detail.

The ESR absorption of a single crystal of $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\cdot-}$ and its variation with the temperature were measured for three arbitrary orientations. Figure 1 shows the experimental results for one of the orientations. Striking temperature effects were found in the ESR spectra. At low temperatures (approximately at 112 K), doublet components of the triplet-state fine structure and a central paramagnetic impurity signal[26)] were observed. The doublet components are sharp (about 0.7_0 gauss in width) and well-resolved. These doublet components, the separation of which is quite anisotropic, arise from the zero-field splitting of the triplet state in the absence of the triplet exciton exchange.[1)] As the temperature is raised, the doublet components broaden and move together, eventually collapsing into a single line which becomes progressively sharper, approaching a limit of about 1.9_0 gauss in width at room temperature;[27)] these changes were found to be thermally reversible. This spectroscopic behavior is characteristic of an exchange interaction, a process which first removes the fine structure (exchange broadening) and then sharpens up the single remaining resonance line (exchange narrowing).

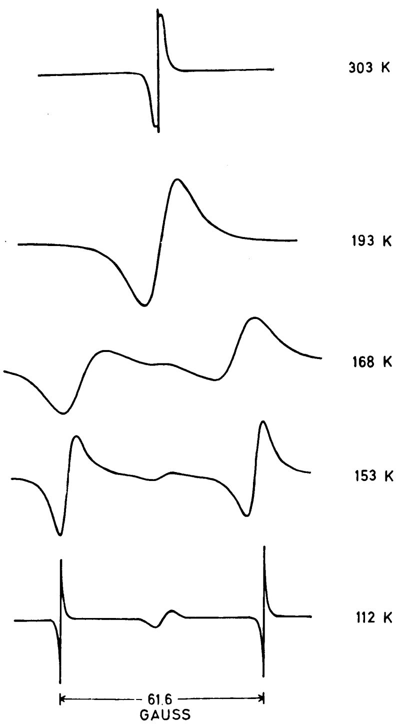

Fig. 1. The temperature dependence of the ESR absorption of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\cdot-}$ salt for the d_0=61.6 gauss orientation. The spectra were obtained with different spectrometer gain settings at the different temperatures.

Figure 2 demonstrates the temperature dependence of the ESR spectra of the same salt for another orientation, where the separation of the fine-structure splitting at low temperature is narrower than that in Fig. 1. In this case, the temperature at which the doublet components collapse into a single line was found to be lower than that in Fig. 1. However, the line-widths of the absorptions at the low and high temperature limits were practically the same as those in Fig. 1.

Discussion

There have been various treatments of exchange-narrowing phenomena in magnetic resonance spectra.[28,29)] Jones and Chesnut have applied Bloch equa-

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[25)] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

[26)] The ESR absorption intensity of the central absorption decreased, as the temperature was raised, according to the Curie law.

[27)] It was noticed that, in addition to the exchange-narrowed absorption, a sharp spike of absorption appeared in the room-temperature ESR spectra. However, no such sharp spike was observed when another smaller crystal was taken as a specimen. The extra absorption may arise from some skin effect, since this material is known to show high electrical conduction.

[28)] H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953); H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956); H. M. McConnell, *ibid.*, **28**, 430 (1958); L. H. Piette and W. A. Anderson, *ibid.*, **30**, 899 (1959).

[29)] P. W. Anderson, *J. Phys. Soc. Jap.*, **9**, 316 (1954); D. Kivelson, *J. Chem. Phys.*, **27**, 1087 (1957).

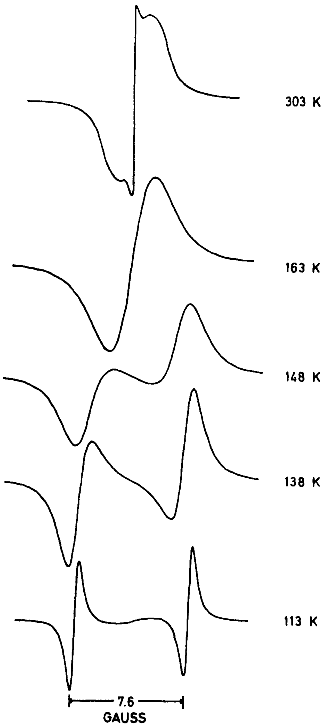

Fig. 2. The temperature dependence of the ESR absorption of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\bar{\cdot}}$ salt for the $d_0=7.6$ gauss orientation.

tions modified to include the effect of exchange to the systems of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\bar{\cdot}}$, $(x=0.00)$, and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\bar{\cdot}}$, $(x=1.00)$,[4] which show two-line spectra arising from the zero-field splitting of $S=1$ species. In the following discussion, we shall also examine the exchange effects of the triplet state in the mixed crystals by applying this method to $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\bar{\cdot}}$, $(x=0.80)$, and will compare them with those for the regular crystal lattices for $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\bar{\cdot}}$ and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\bar{\cdot}}$.

For the ESR absorption of the simple two-line case, we can express the line separation, d, and the line width, ΔH, in terms of the exchange frequency, ν. For the slow exchange region $(d_0 \gg \sqrt{2}\,\nu/\gamma)$:

$$\gamma^2(d_0^2-d^2) = 2\nu^2, \tag{1}$$

$$\gamma(\Delta H-\Delta H_0) = \nu/\sqrt{3}, \tag{2}$$

while for the fast exchange region $(d_0 \ll \sqrt{2}\,\nu/\gamma)$:

$$2\sqrt{3}(\Delta H-\Delta H_0) = \gamma d_0^2/\nu, \tag{3}$$

$$d = 0, \tag{4}$$

where ΔH and ΔH_0 are the linewidths in gauss measured from the points of maximum slope of the first derivative of the absorption in the presence and in the absence of exchange respectively. d and d_0 are the separation of the two lines in gauss with and without exchange respectively, and γ is the gyromagnetic ratio of the electron. These equations demonstrate that, when the exchange frequency is increased, each of the two spectral lines broadens and shifts towards the center of the spectrum, and then the two lines collapse into a single broad line, which becomes progressively sharper. The limiting line width in both extremes is given by ΔH_0.

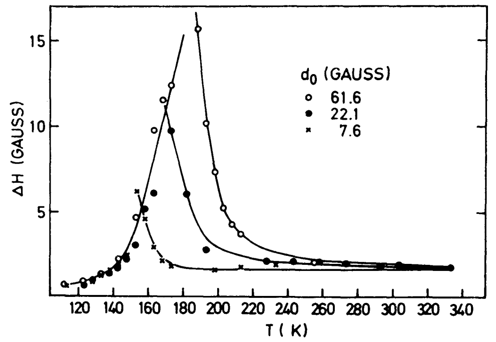

Fig. 3. Plots of line width of the ESR absorption *versus* temperature in K for various orientations of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\bar{\cdot}}$ salt.

These theoretical features agree well with those of our experimental results in Fig. 3, which shows the line-width measurements of the ESR absorptions of $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\bar{\cdot}}$, $(x=0.80)$, as functions of the temperature (and, thus, of the exchange frequency) for several crystal orientations (different values of d_0). The various curves in Fig. 3 intersect at the point where $\nu=\gamma d_0$. In the left region of this point (in the lower temperature region), we observed a two-line spectrum for slow exchange, but in the right region (in the higher temperature region), we observed a single-line spectrum for fast exchange. The application of the above simple two-line analysis to our experimental results is supported by the fact that the intersection at $\nu=\gamma d_0$ takes place at lower temperatures as d_0 is decreased and that, in the slow-exchange region, ΔH is found to depend only on the temperature.

For $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\bar{\cdot}}$, $(x=0.80)$, the values of the exchange frequencies, ν, were determined from the observed ESR spectra as a function of the temperature. For three crystal orientations, the calculations were made by the use of the approximations expressed by Eqs. (1), (2), and (3) respectively. The values of d_0 were taken as the limiting values of d at low temperatures. ΔH_0 was taken in a similar way, using the high- or low-temperature limits. For the three d_0 orientations, the estimated values of ν *versus* the temperature are illustrated in Figs. (4)—(6), in which the signs of $\nu(1)$, $\nu(2)$, and $\nu(3)$ indicate the values estimated by using Eqs. (1), (2), and (3) respectively.

In general, it was found that a good linear relation was obtained when the logarithm of the exchange frequency was plotted against the reciprocal of the absolute temperature. Therefore, the exchange frequency, ν, was described by:

$$\nu = \nu_0 \exp(-\Delta E/kT), \tag{5}$$

where ΔE is the activation energy for exchange. The parameters of ν_0 and ΔE were determined from the slow-exchange line collapse of Eq. (1), the slow-exchange line broadening of Eq. (2), and the fast-exchange line narrowing of Eq. (3). They are denoted as $\nu_0(i)$ and $\Delta E(i)$ $(i=1$, 2, and 3) respectively. The estimated values are collected in Table 1, together with those for

TABLE 1. EXCHANGE PARAMETERS OF $\nu_0(i)$ AND $\Delta E(i)$, (i=1, 2, AND 3), FOR THE ANION RADICAL SALTS OF $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, ($0 \leq x \leq 1$)[a)]

Composition parameter, x	d_0 (gauss)	$\nu_0(1)$ (Hz)	$\Delta E(1)$ (eV)	$\nu_0(2)$ (Hz)	$\Delta E(2)$ (eV)	$\nu_0(3)$ (Hz)	$\Delta E(3)$ (eV)	Reference
0.80	7.6	5.6×10^{10} (±2.0)	0.11 (±0.01)	1.6×10^{13} (±0.9)	0.20 (±0.01)	—	—	This work
	22.1	5.4×10^{11} (±2.3)	0.14 (±0.01)	2.9×10^{13} (±1.1)	0.22 (±0.02)	1.5×10^{13} (±3.9)	0.19 (±0.02)	This work
	61.6	4.0×10^{9} (±1.4)	0.048 (±0.003)	9.2×10^{11} (±2.1)	0.15 (±0.01)	1.4×10^{13} (±3.6)	0.17 (±0.02)	This work
0.00	—	1.4×10^{10} (±0.2)	0.042 (±0.001)	1.6×10^{12} (±0.9)	0.13 (±0.01)	5.4×10^{14} (±4.6)	0.19 (±0.01)	4
1.00	—	2.8×10^{10} (±1.2)	0.050 (±0.007)	3.5×10^{12} (±4.8)	0.11 (±0.02)	3.3×10^{13} (±2.5)	0.16 (±0.01)	4

a) The values of $\nu_0(i)$ and $\Delta E(i)$, (i=1, 2, and 3), were derived from Eqs. (1), (2), and (3), respectively.

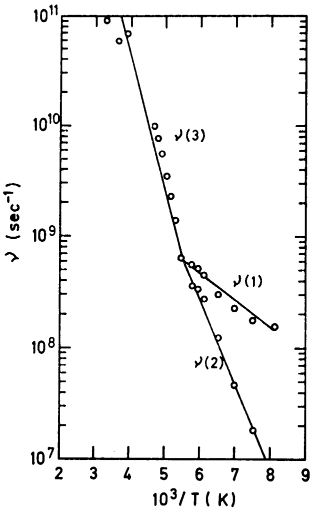

Fig. 4. Semilog plot of ν *versus* $1/T$ K for the d_0=61.6 gauss orientation of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\dot{-}}$ salt. $\nu(1)$, $\nu(2)$, and $\nu(3)$ indicate the values derived from Eqs. (1), (2), and (3), respectively.

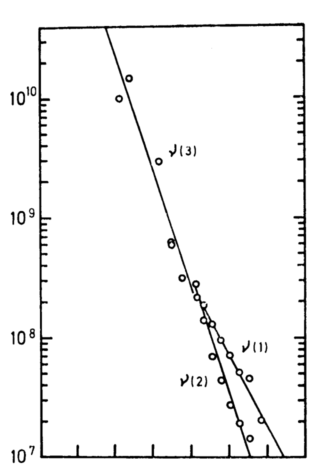

Fig. 5. Semilog plot of ν *versus* $1/T$ K for the d_0=22.1 gauss orientation of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^{\dot{-}}$ $(TCNQ)_2^{\dot{-}}$ salt.

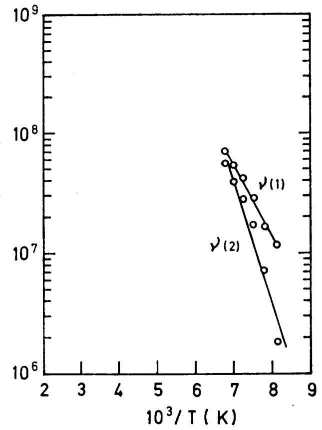

Fig. 6. Semilog plot of ν *versus* $1/T$ K for the d_0=7.6 gauss orientation of a single crystal of the $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\dot{-}}$ salt.

the salts of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, (x=0.00), and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, (x=1.00).[4)] These parameters were obtained by the method of least-squares. For the d_0=7.6 gauss orientation, however, we could scarcely determine the $\nu_0(3)$ and $\Delta E(3)$ values, since the estimation of $\nu(3)$ *versus* the temperature could not be made over the wide temperature range.

For $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\dot{-}}$, (x=0.80), the data given in Table 1 show that $\Delta E(3) \gtrless \Delta E(2) > \Delta E(1)$ and $\nu_0(3) \geq \nu_0(2) > \nu_0(1)$. As has been pointed out by Jones and Chesnut,[4)] for the exchange effect of the triplet exciton system, the simple two-site exchange model may yield different ν_0 and ΔE values, depending on whether one uses Eqs. (1), (2), or (3). This is also shown by the experimental results we give in Table 1. Rigorously speaking, according to the calculations by Lynden-Bell,[30)] the simple two-site model is not always applicable to the triplet-exciton system. However, for purposes of comparison with those for $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$ and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, the simple two-site analysis was applied to the present case. Except for the small d_0 crystal orientation, the values of $\nu_0(i)$ and $\Delta E(i)$ (i=1, 2, and 3) in $[(C_6H_5)_3PCH_3]_{0.20}^+$ $[(C_6H_5)_3AsCH_3]_{0.80}^+$ $(TCNQ)_2^{\dot{-}}$ were found to coincide well

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[30)] R. M. Lynden-Bell, *Mol. Phys.*, **8**, 71 (1964).

with those for the regular crystal lattice in $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ or $[(C_6H_5)_3AsCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ respectively, within the limits of experimental error.[4] The apparent values of $\Delta E(i)$ $(i=1, 2, \text{and } 3)$ were found to be somewhat anisotropic; larger values of $\Delta E(i)$ were obtained for the smaller d_0 crystal orientation. As d_0 approaches zero, however, the straight application of Eqs. (1)—(3) may cause apparent ΔE anisotropy, since one can hardly measure the linewidth accurately because of the overlap of the two lines.

The exchange effect of the triplet state can be understood in terms of the movement of pseudo-particles with spin 1 (*i.e.*, triplet excitons). The ESR spectra of the triplet excitons do not show any hyperfine structure, even at low temperatures, since their mobility causes its motional narrowing. At higher temperature, as the concentration of the excitons is increased, the mutual collisions of the triplet excitons lead to an exchange-narrowing effect of the triplet-state fine structure. Thus, we can relate the exchange frequency, ν, to the collision frequency of the triplet excitons:

$$\nu \propto n\sigma v, \tag{6}$$

where n is the concentration of triplet excitons; v, an average propagation velocity, and σ, an effective cross-section for triplet-exciton collisions. For our system below room temperature, we can approximately take:

$$n \propto [\exp(J/kT)+3]^{-1} \approx \exp(-J/kT), \tag{7}$$

where J is the energy difference between the singlet ground state and the triplet excited state. According to Kepler's susceptibility measurements,[6] $J=0.065$ eV below room temperature for the salts of $[(C_6H_5)_3PCH_3]_{1-x}^+ [(C_6H_5)_3AsCH_3]_x^+ (TCNQ)_2^{\overline{\cdot}}$, $(0 \leq x \leq 1)$. Judging from our experimental expression of $\nu=\nu_0 \exp(-\Delta E/kT)$ for the salt with $x=0.80$, the $\Delta E \approx J$ equality should exist if we assume that σ and v are not strongly temperature-dependent. However, our experimental results given in Table 1 show this correlation not to be generally correct. In general, $\Delta E(1)$, $\Delta E(2)$, $\Delta E(3) > J$, except $\Delta E(1) < J$ for the $d_0=61.6$ gauss crystal orientation. Jones and Chesnut have considered that ΔE might exceed J if the propagation of the triplet exciton could involve an activated process (*i.e.*, a diffusional propagation) with an activation energy of $\Delta E_v = \Delta E - J$, that is:[4]

$$v \propto \exp(-\Delta E_v/kT). \tag{8}$$

In this case, the foregoing anisotropy of the ΔE values, if it exists, seems to be attributable to that of the ΔE_v values.

According to the X-ray diffraction studies by McPhail *et al.*,[31] the crystal structures of both $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ and $[(C_6H_5)_3AsCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ are triclinic and isomorphous.[32] The planar TCNQ molecules are stacked face-to-face to form a column along the b-axis. Four TCNQ molecules form a repeating unit in the column. The ion radius of the arsonium cation is somewhat longer than that of the phosphonium cation. It is almost certain that the crystal structures of the salts containing the mixed cations are identical with that of the phosphonium or arsonium salt. This kind of molecular stacking should then lead to anisotropic ΔE_v values if the triplet exciton can be described by the diffusional process. At present, a question remains in which crystal direction the activation energy, ΔE_v, has its maximum and minimum values.

Up to now, extensive investigations have been made to distinguish whether or not the triplet excitons in ion radical salts can be characterized by "localized excitons" or "free excitons."[7,8,13–16] The localized exciton carries a distortion with it as it goes through the crystal lattice. The exciton motion is, then, represented by a hopping from one cell to the next through a random walk (*i.e.*, diffusional process). On the other hand, the free exciton goes through the crystal lattice, carries with it essentially no crystal distortion, and has a long mean free path. The free exciton is, then, expressed by extended wave packets distributed over the whole lattice. In the salts containing mixed cations, if the mixed cations are randomly arranged, the crystal lattices will no longer be periodic. In this case, the free excitons are strongly scattered by the irregular crystal lattices, while the localized excitons are not. The present ESR experimental results support the model of localized triplet excitons, since the observed ν_0 and ΔE values for $[(C_6H_5)_3PCH_3]_{0.20}^+ [(C_6H_5)_3AsCH_3]_{0.80}^+ (TCNQ)_2^{\overline{\cdot}}$ coincide well with those in the regular crystal lattices for $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ and $[(C_6H_5)_3AsCH_3]^+ (TCNQ)_2^{\overline{\cdot}}$ respectively.[4] Soos and McConnell have found that the activation energy for diffusion, ΔE_v, is essentially $\Delta/2$ where Δ is the "self-trapping energy" of the triplet exciton due to exciton-phonon interaction.[14] These results suggest that, at least in the anion radical salts of $[(C_6H_5)_3PCH_3]_{1-x}^+ [(C_6H_5)_3AsCH_3]_x^+ (TCNQ)_2^{\overline{\cdot}}$, $(0 \leq x \leq 1)$, the best picture of the triplet-exciton motion is one in which a localized exciton rapidly hops from one site to the next. The motion is, then, "random walk" or diffusional.

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[31] A. T. McPhail, G. M. Semeniuk, and D. B. Chesnut, *J. Chem. Soc., A*, **1971**, 2174.

[32] The electronic state and the crystal properties of the phosphonium salt are very similar to those of the arsonium salt, except for the occurrence of the phase transition of the phosphonium salt at 315.7 K. See Refs. 1,2,4–6,9–11,16,19–24.