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THE RELATIONSHIP BETWEEN MICROWAVE SPECTROSCOPY, COHERENT TRIPLET EXCITONS,  
AND DENSITY OF STATES FUNCTIONS IN MOLECULAR CRYSTALS

by

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Abstract

A theory for microwave band-to-band transitions in triplet Frenkel excitons in the coherent migration limit for a one-dimensional exciton associated with translationally equivalent molecules is developed. Because of selective spin-orbit coupling to the magnetic sublevels, an anisotropy in the zero field splitting across the band ( $k = 0$  to  $k = \pm \pi/a$ ) occurs which, on a reduced energy scale, "mirrors" the energy dispersion of triplet exciton states. As a result, if the coherence time of a  $k$  state of the triplet band is longer than the intrinsic time associated with a microwave field connecting the magnetic sublevels of the band, one can measure both the bandwidth and density of states function with a zero field electron spin resonance experiment.

<sup>†</sup> Alfred P. Sloan Fellow

## 1. Introduction

The dynamical properties of energy transport in molecular crystals has been a problem of considerable interest. <sup>(1)</sup> Because the long lifetime of triplet states allows extensive energy transfer over long distances with reasonably small intermolecular interactions, the migration of Frenkel triplet excitons is particularly important. Despite extensive experimental and theoretical work by many authors an adequate understanding of the basic mechanism of migration is far from being realized. The problem rests in properly treating exciton-phonon coupling, vibrational coupling between adjacent molecules and exchange coupling between electronic states on adjacent molecules.

An interesting feature, however, of energy migration, exciton or polaron, is the prediction of coherent motion in a narrow band of the molecular crystal at certain temperatures. <sup>(2)</sup> The importance of coherent motion is that the exciton states are delocalized over much greater distances than in the incoherent or "hopping model" and consequently long range interactions can become extremely important in directing physical phenomena associated with the exciton, e.g., exciton-exciton annihilation <sup>(3)</sup> exciton-trap interactions, <sup>(4)</sup> etc. The quantitative temperature and band width dependence of coherent transport depends explicitly upon the scattering model adopted. For instance, in Holstein's <sup>(2,5)</sup> self trapping polaron model which assumes linear electron-phonon interactions, <sup>(6)</sup> the loss of coherence is characterized by a transition temperature above which the incoherent or hopping motion best describes the transport

phenomena. The same is true in the quadratic-electron-phonon interaction recently developed by Siebrand;<sup>(7)</sup> however, the explicit temperature dependence differs in the two models, the latter having broader intermediate temperature regions where both processes contribute to migration.

It is not the purpose of this preliminary communication to differentiate the various models for exciton-phonon interactions, but rather to develop the theory of microwave transitions between the triplet magnetic sublevel exciton bands in molecular crystals in the one-dimensional case for coherent triplet exciton migration. In the following paper we will demonstrate experimentally the observation of coherent migration of triplet excitons at low temperatures in a molecular crystal (1,2,4,5 tetrachlorobenzene) which represents the one dimensional case.<sup>(8)</sup> In a later publication we will extend the concepts and experimental techniques developed here to the intermediate case between coherent and incoherent migration in an attempt to look explicitly at the temperature dependence of the phonon-exciton scattering.

## 2. The Relationship between Microwave Transition Frequency and the Energy Dispersion of a Triplet Band

To properly consider a one-dimensional triplet band, account must be taken of the magnetic sublevels of the triplet state.<sup>(9)</sup> By representing the molecular wavefunctions of the triplet state as the spin-orbit functions,  $\phi^p$ ,

$$\phi^p = |\psi^\Gamma \cdot \tau_p\rangle \quad (p = x, y, z), \quad (1)$$

where  $\psi^\Gamma$  represents the triplet orbital function of  $\Gamma$  symmetry and  $\tau_p$  represents the spin function of the  $p^{\text{th}}$  magnetic sublevel, it is clear that the total symmetry of  $\phi^p$  ( $p = x, y, z$ ) transforms as the irreducible representation of the direct product  $\Gamma \times R_p$ , where  $R_p$  ( $p = x, y, z$ ) are the rotation operators of the molecular point group. In  $D_{2h}$  for instance, all three of the molecular spin-orbit wave functions must be of different symmetry. In the absence of spin-orbit coupling of a triplet with the singlet states, the magnetic sublevels are split only by the electron dipole-dipole interactions.<sup>(10)</sup> These splittings are the well known zero field splittings. Because electron exchange is the dominating mechanism for energy migration in triplet excitons<sup>(1,11)</sup> and because exchange is a totally symmetric operator, the delocalized states of the crystal, specifically the triplet exciton band, can be formed from each of the individual magnetic sublevel spin-orbit functions separately in the absence of spin-orbit coupling. Thus, the triplet exciton band for a one-dimensional exchange interaction between translationally equivalent molecules is in zero order three parallel bands whose separations are related to the conventional molecular zero field splitting parameters<sup>(10)</sup>  $D$  and  $E$  as illustrated in Figure 1a. The intermolecular effective electron exchange interaction  $\beta$ , in the one-dimensional model<sup>(12)</sup> is simply related to the band width  $2\Delta_T$  as

$$2\beta = \Delta_T \quad (2)$$

and the energy dependence in the wave vector,  $k$ , in the first Brillouin Zone of a one-dimensional band with intermolecular interaction along the a direction is

$$E^p(k) = E^0 - \Delta_T(\cos ka) + E^p \quad (p = x, y, z), (k = 0, \pm 1, \dots \pm \pi/a) \quad (3)$$

where  $E^0$  is the ground state singlet-triplet energy separation of the molecule in the crystal environment in the absence of intermolecular exchange and corresponds to the band energy at  $k = \pi/2a$ .  $E^p$  is related to the triplet zero field splittings as:

$$E^x = 1/3 D + E, \quad (4a)$$

$$E^y = 1/3 D - E, \quad (4b)$$

$$E^z = -2/3 D. \quad (4c)$$

It should be noted (cf. Figure 1), that in the absence of a magnetic field the triplet bands are symmetric around  $k = 0$  because of time reversal symmetry. (13)

We have assumed thus far spin-orbit basis functions, however we have excluded spin-orbit coupling per se. It is generally recognized that in molecules such as azaaromatics and halogenated aromatics the primary mechanism for phosphorescence is via selective spin-orbit coupling of one or more of the triplet sublevels with the excited singlet states. (14)

This implies naturally that there will be a small but finite spin-orbit contribution to the zero field splittings in the molecular states of the triplet. (15) In the delocalized states of molecular crystals, because singlet exciton bands have bandwidths 10 to 100 times those for triplet bands, (1) one expects spin-orbit coupling to be  $k$  dependent. Assuming for the moment that only one magnetic sublevel band, say  $z$ , spin-orbit couples with a singlet band whose bandwidth is  $2\Delta_S$ , the contribution of spin-orbit coupling to  $E^z(k)$  can be treated via perturbation theory.



Specifically,

$$E^z(k) = E^0 - \Delta_T(\cos ka) + E^D + E_{SO}^z(k), \quad (5)$$

where the spin-orbit contribution

$$E_{SO}^z(k) = -\xi^2 / \left( E_{ST}^0 + (\Delta_S - \Delta_T) \cos ka \right). \quad (6)$$

$E_{ST}^0$  is the singlet-triplet separation in the absence of intermolecular interactions and  $\xi$  is the molecular spin-orbit coupling coefficient. Expanding Eq. (6) in a binomial series, we obtain

$$E_{SO}^z(k) = -\xi^2 / E_{ST}^0 \left( 1 - \left[ \frac{(\Delta_S - \Delta_T)}{E_{ST}^0} \right] \cos ka + \left[ \frac{(\Delta_S - \Delta_T)}{E_{ST}^0} \right]^2 \cos^2 ka - \dots \right). \quad (7)$$

The leading term is simply the spin-orbit contribution in the absence of intermolecular interactions. To within one percent for reasonable values of  $\left[ \frac{\Delta_S - \Delta_T}{E_{ST}^0} \right]$ , say 0.1 to 0.01, the series can be terminated after the first power of  $\cos ka$ .<sup>‡</sup> The effect of selective spin-orbit coupling in the first Brillouin Zone of the triplet bands is illustrated in Figure 1b.

In spite of the small contribution of spin-orbit coupling to the energy of the z magnetic sublevel of the triplet band,  $E^z(k)$ , its importance can not be underestimated, for in a one-dimensional model it provides an anisotropy in the energy difference between two magnetic sublevels, say  $E^z(k)$  and  $E^y(k)$ , which reflects the overall energy dispersion in  $k$  of the triplet band itself. Expressed more formally,

$$\Delta E^{yz}(k) = E^y(k) - E^z(k); \quad (8)$$

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<sup>‡</sup> Considering spin-orbit coupling rigorously in the wavefunctions forming the basis functions for the delocalized states of the crystal results directly in an energy dependence,  $E_{SO}^z$ , linear in  $(\Delta_S - \Delta_T) \cos ka$ .

in much the same way as chemical exchange averages microwave or NMR transitions.<sup>(18)</sup> The temperature dependence of  $\Delta E_j^{yz}(k)/\hbar$  thus provides, in principle, a method for distinguishing different phonon-exciton scattering models. This will be discussed in a later publication.

In the coherent model, however, assuming a coherence lifetime  $\tau(k) > (\hbar/\Delta E^{yz})$ , we expect a broad line whose frequency reflects the  $k$  dependent energy dispersion of the band. Next we must consider the intensity of  $\Delta E_1^{yz}(k)/\hbar$  as a function of  $k$ .

### 3. The Relationship of the Microwave Transition Intensity to the Density of States Function of the Band

To accurately treat the intensity of a band-to-band microwave transition in a triplet exciton requires a quantitative evaluation of the distribution of exciton states in the three magnetic sublevel bands, including spin lattice relaxation effects, spin-spin relaxation phenomena, and many other terms. The problem can be greatly simplified by several physically reasonable assumptions. First, we will assume that the coherence time of a  $k$  state,  $\tau(k)$ , is longer than the intrinsic microwave time,  $\hbar/\Delta E^{yz}(k)$  but shorter than both the lifetime of the exciton and the spin lattice relaxation time between magnetic sublevels. It is highly unlikely that  $\tau(k)$ , for triplet excitons at 4.2°K, would be as long as several milliseconds, which is a value typical for short lived phosphorescent triplet states in the halogenated benzenes. Spin lattice relaxation times at 4.2°K for triplet states in the absence of magnetic fields also have millisecond values. This assumption is tantamount to Boltzmannizing

independently via  $k$  scattering the individual magnetic sublevels,  $E^p(k)$ , within both the lifetime of the exciton and the spin lattice relaxation time, the Boltzmann distribution being taken over the ensemble of  $N$  identical one-dimension exciton chains.

In terms of the number of identical chains  $N$ , the magnetic sublevel populations  $N^p(E)$  are related as  $N = \sum_p N^p(E)$ , where  $E = E^p(k)$ .

Secondly, we will assume that  $N^p(E)$  for all  $p$  (i.e.,  $x$ ,  $y$ , and  $z$ ) are functionally the same in  $k$ . Expressed another way, because the spin-orbit perturbation is small compared to the bandwidth  $2\Delta_p$ , we need not concern ourselves with small corrections in the population differences between magnetic sublevels arising from  $k$  dependence of the zero field splitting. With these two assumptions the populations corresponding to energies  $E^p(k)$  ( $p = x, y, z$ ) differ from one another by a constant. Formally,

$$C^x N^x(E) = C^y N^y(E) = C^z N^z(E), \quad (19)$$

where the constants  $C^p$  ( $p = x, y, z$ ) are related to electron spin alignment via selective intersystem crossing and phosphorescence emission from the individual magnetic sublevels of the band and spin lattice relaxation between the sublevels. The explicit features of the  $C^p$ 's will not be discussed at this point.

With these assumptions the relationship of the individual sublevel populations of  $N^p(E)$ , to the band, is simply the density of states functions of the bands related only to  $2\Delta_p$  times the Boltzmann factor, i.e.,

$$N^p(E) = C^p D^p(E) e^{-E/kT}, \quad (20)$$

where  $E = \Delta_T(1 - \cos ka)$  and  $D'(E)$  is the density of states function for a one-dimensional band including the Van Hove singularities. (19)

The removal of the Van Hove singularities can be achieved simply and without specifying an explicit phonon scattering parameter by a Gaussian or Lorentz broadening function. (20) Using the Van Hove density of states function for a one-dimensional exciton and the Boltzmann factor, the broadened Boltzmann density of states function,  $D^B(E)$  is simply

$$D^B(E) = \frac{\delta}{\pi} \int_0^{2\Delta_T} \frac{D'(E') \exp(-E'/kT)}{(E - E')^2 + \delta^2} dE' \quad (21a)$$

or

$$D^B(E) = \sqrt{\frac{\ln 2}{\pi\delta}} \int_0^{2\Delta_T} D'(E') \exp(-E'/kT) \exp[-(E - E')^2 \ln 2/\delta^2] dE' \quad (21b)$$

where  $\delta$  is the Lorentz [Eq. (21a)] or Gaussian [Eq. (21b)] scattering parameter.

The relation of a density of states function across the band  $2\Delta_T$  to the microwave band-to-band energy  $\Delta E_1^{yz}(E)$  with the above assumptions is simply

$$D^B[\Delta E_1^{yz}(E)] = \frac{\delta^\omega}{\pi} \int_0^{\pi/a} \frac{\exp[\Delta_T(1 - \cos ka)/kT] dk}{[\Delta E_1^{yz}(E) + \Delta_{ST} \cos ka]^2 + (\delta^\omega)^2} \quad (22a)$$

or

$$D^B [\Delta E_1^{yz}(E)] = \sqrt{\frac{\ln 2}{\pi \delta^\omega}} \int_0^{\pi/a} \exp\left[\frac{\Delta_T(1 - \cos ka)}{kT}\right] \cdot \exp\left(-\left[\Delta E_1^{yz}(E) + \Delta_{ST}^{\xi} \cos ka\right]^2 \ln 2 / \delta^\omega\right) dk \quad (22b)$$

This equation arises from substitution of Eq. (16) into Eq. (21 a or b) where  $\delta^\omega$  is related to the reduction factor  $f$  by  $f\delta = \delta$ .

The significance of Eqs. (22 a and b) is that the intensity of a microwave band-to-band  $I(E)$  transition as a function of  $\Delta E_1^{yz}(E)$  is directly related to the Boltzmannized density of states of the triplet band or

$$I [\Delta E_1^{yz}(E)] \sim D^B [\Delta E_1^{yz}(E)] \quad (23)$$

$$I [\Delta E_1^{yz}(E)] = C D^B (E), \quad (24)$$

where  $C$  is some experimental constant.

It thus becomes possible to determine experimentally both the density of states function and the bandwidth of a one-dimensional triplet exciton when the coherence time of the  $k$  state is longer than the reciprocal microwave frequency.

Figure 2 illustrates

$I [\Delta E^{yz}(E)]$  vs  $\Delta E^{yz}(E)$  for various bandwidth-temperature ratios,  $2\Delta_T/T$ , while Figure 3 shows the variation on scattering at 4.2° K with a band width  $2\Delta_T = 2 \text{ cm}^{-1}$ . (21)

#### 4. Summary

In the limit where exciton scattering is sufficiently weak to allow the lifetime of a  $k$  state in a triplet exciton to be longer than the reciprocal microwave frequency associated with the zero field magnetic sublevels of the band:

(a) the microwave frequency is directly related to the triplet band dispersion in one dimension;

(b) the intensity of the microwave transition is related to the density of states function of the band times a Boltzmann factor.

Thus, the bandwidth and density of states can be determined directly by a zero field microwave experiment.

It should also be noted that once the triplet bandwidth  $2\Delta_T$  is determined the contribution of spin-orbit coupling to the zero field splitting can be calculated from the reduction factor  $f$  since in one dimension the microwave frequency at  $k = 0$  and  $k = \pi/a$  is experimentally known.

#### 5. Acknowledgements

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References

1. S. A. Rice and J. Jortner, Physics and Chemistry of the Organic Solid State, Vol. 3 (Interscience, N. Y., 1957).
2. A. S. Davydov, Theory of Molecular Excitons (McGraw Hill, N. Y., 1962), and T. Holstein, Ann. Phys. (N.Y.) 8, 325 (1959).
3. P. A. Avakian and R. E. Merrifield, Mol. Cryst. 5, 37 (1968); R. E. Merrifield, J. Chem. Phys. 48, 4318 (1968); R. C. Johnson, R. E. Merrifield, P. Avakian and R. B. Flippen, Phys. Rev. Letters 19, 285 (1967); R. P. Groff, R. E. Merrifield and P. Avakian, Chem. Phys. Letters 5, 168 (1970).
4. G. C. Nieman and G. W. Robinson, J. Chem. Phys. 37, 2150 (1962); H. Sternlicht, G. C. Nieman, and G. W. Robinson, J. Chem. Phys. 38, 1326 (1963); S. D. Colson and G. W. Robinson, J. Chem. Phys. 48, 2550 (1968).
5. T. Holstein, Ann. Phys. (N.Y.) 8, 343 (1959).
6. Silbey has also treated the one dimensional case using a linear exciton-phonon interaction, R. Silbey, Private communication.
7. R. W. Munn and W. Siebrand, J. Chem. Phys. 52, 47 (1970).
8. A. H. Francis and C. B. Harris, Chem. Phys. Letters, \_\_, XXX (1971).
9. Hochstrasser, Clark, and Whiteman have considered the individual magnetic sublevels of exciton bands in interpreting the optical spectra of triplet excitons: R. H. Clarke and R. M. Hochstrasser, J. Chem. Phys. 48, 1745 (1968); R. M. Hochstrasser and J. D. Whiteman, Proc. of Intern. Conf. on Organic Scintillators and Liquid Scint. Counting, San Francisco, July, 1970.

10. A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford, England, 1970).
11. R. E. Merrifield, J. Chem. Phys. 23, 402 (1955).
12. D. P. Craig, Adv. in Chem. Phys. 8, 27 (1964).
13. C. Herring, Phys. Rev. 52, 361 (1937).
14. M. S. de Groot, I. A. M. Hesselmann and J. H. van der Waals, Molec. Phys. 12, 259 (1967).
15. H. F. Hameka, The Triplet State, Ed. A. B. Zahlan (University Press, Cambridge, 1967), and references therein.
16. H. Sternlicht and H. M. McConnell, J. Chem. Phys. 35, 1793 (1961).
17. Z. G. Zoos, J. Chem. Phys. 51, 2107 (1969).
18. H. M. McConnell, J. Chem. Phys. 28, 430 (1958); H. S. Gutowsky, R. L. Vold, and E. J. Wells, J. Chem. Phys. 43, 4107 (1965).
19. L. Van Hove, Phys. Rev. 89, 1189 (1953).
20. W. Heitler, Quantum Theory of Radiation (Oxford University Press, 1967) (3rd edition), p. 70.
21. All points in Figures 2 and 3 were solved by numerical integration of Equation (22b).



Figure Captions

Figure 1a. The energy dispersion of the triplet magnetic sublevel bands in the absence of spin-orbit coupling. The separations between the spin levels are greatly exaggerated for illustrative purposes.

Figure 1b. The energy dispersion of the triplet magnetic sublevel bands in the presence of selective spin orbit coupling to the  $\tau_z$  sublevel. The separations between the spin levels are greatly exaggerated for illustrative purposes.

Figure 2. The microwave intensity vs. frequency of a band to band transition dependence on  $2\Delta_T/T$  with the reduction factor,  $f$ , adjusted to give the same microwave frequency dispersion: (1)  $2\Delta_T/T = 0.25$ , (2)  $2\Delta_T/T = 0.75$ , and (3)  $2\Delta_T/T = 1.50$ . All curves use a Gaussian broadening,  $\delta = 10\%$  of  $2\Delta_T$ .

Figure 3. The microwave intensity vs. frequency dependence on the Gaussian broadening  $\delta$ , with  $2\Delta_T = 2.0$  cm,  $T = 4.2^\circ$  K: (1)  $\delta = 10\%$  of  $2\Delta_T$ , (2)  $\delta = 18\%$  of  $2\Delta_T$ , and (3)  $\delta = 26\%$  of  $2\Delta_T$ .

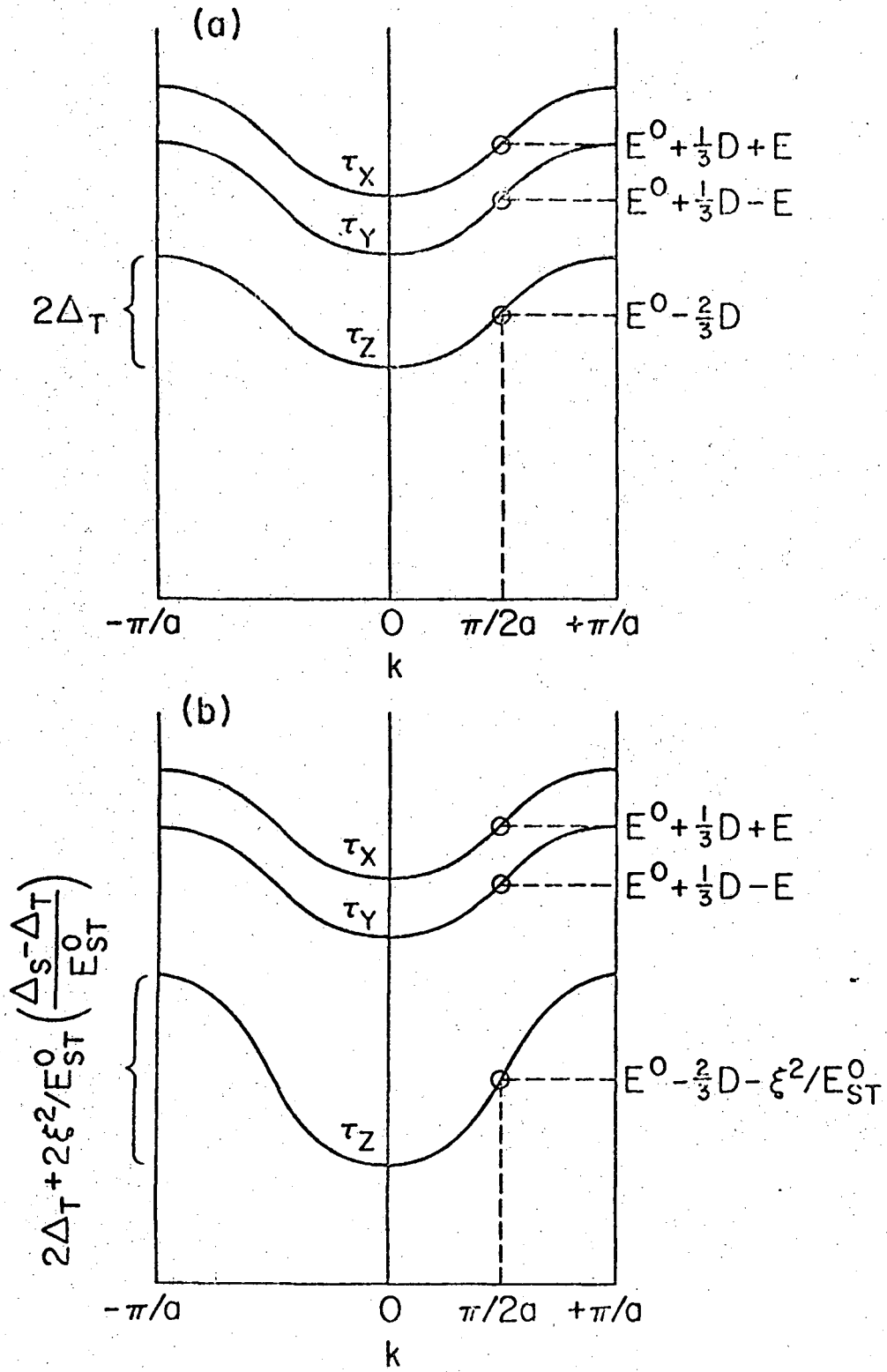


Fig. 1.

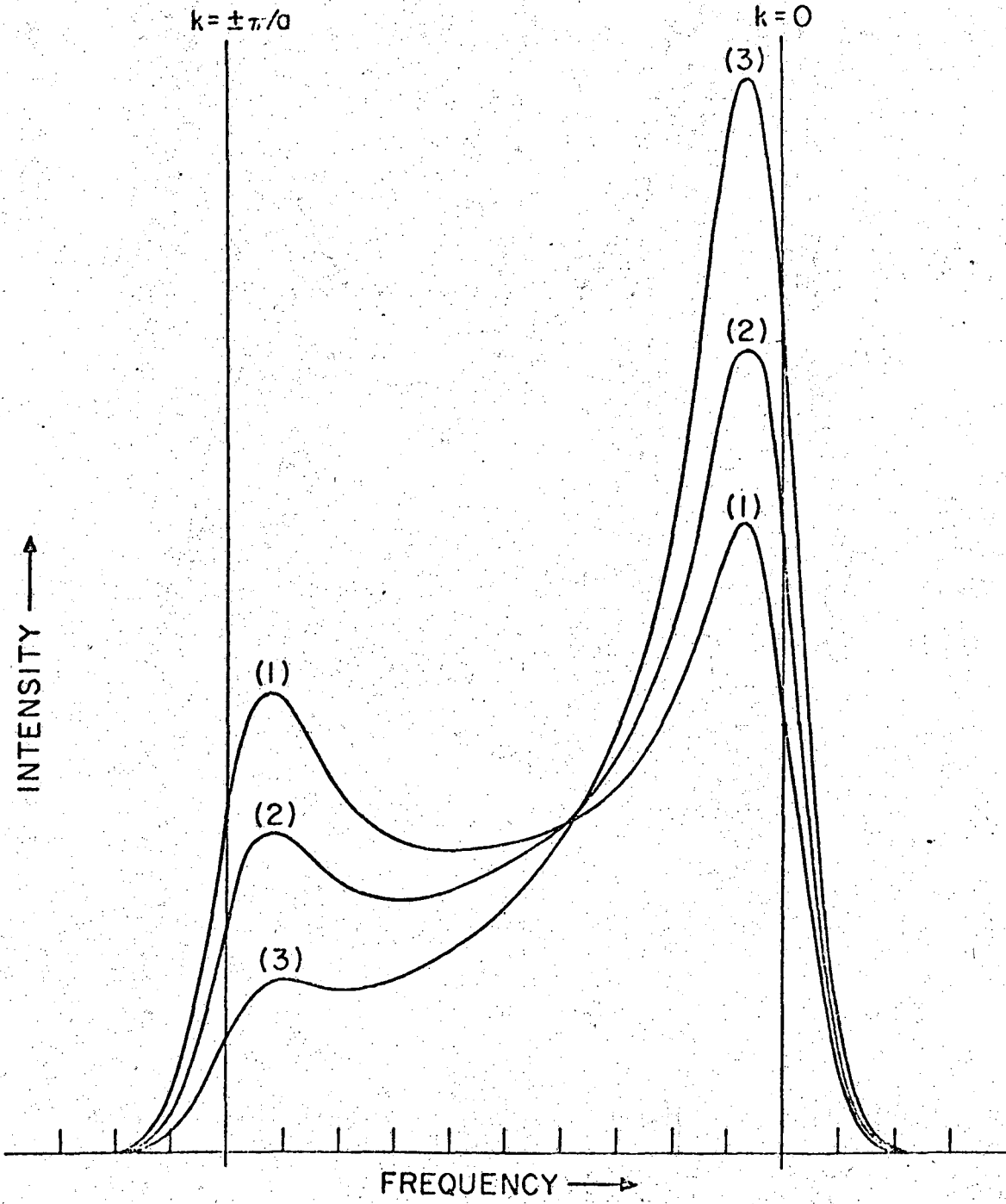


Fig. 2.

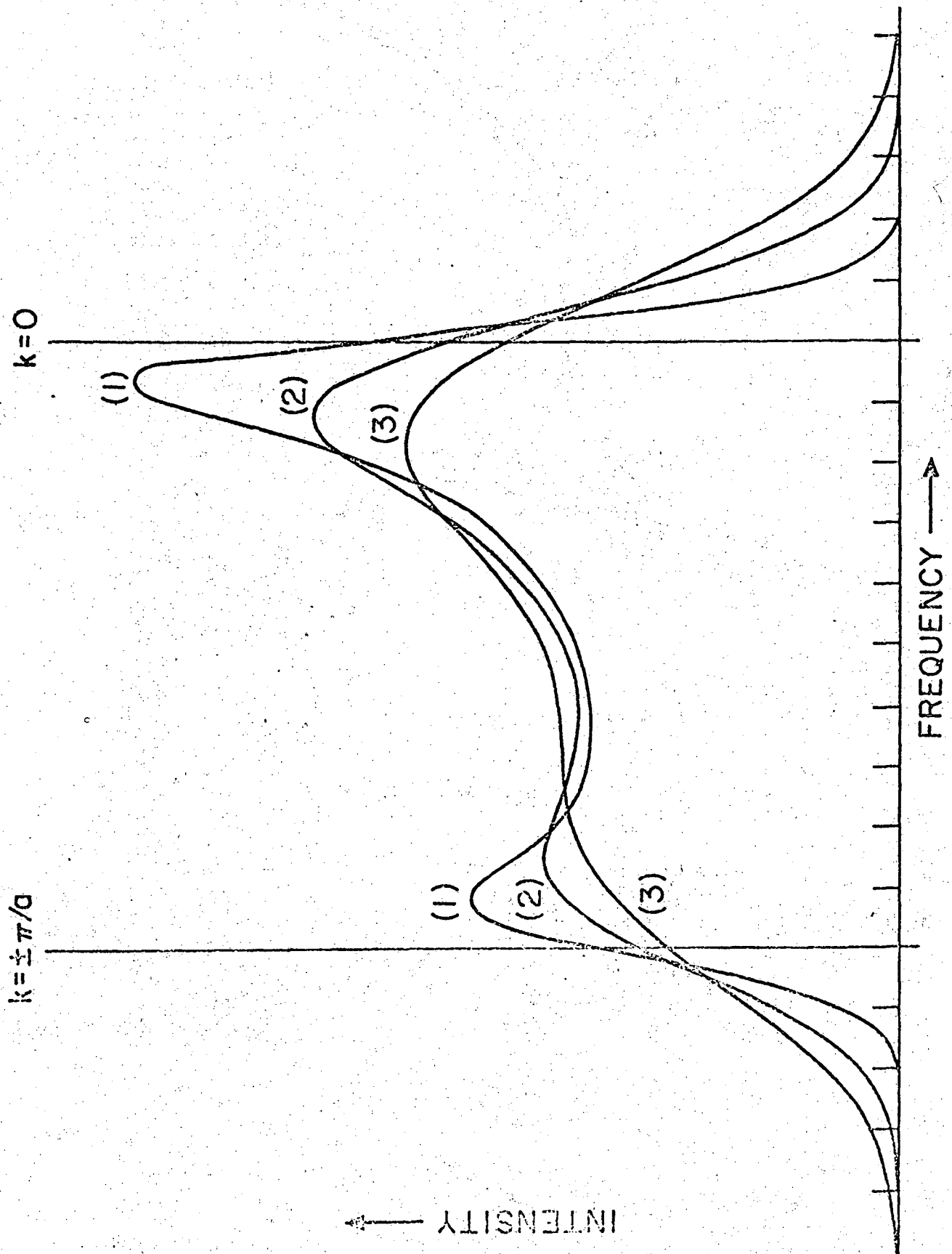


Fig. 3.

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