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## Exciton Energy Transfer in GaP:N

P. J. Wiesner and R. A. Street

*Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany*

and

H. D. Wolf\*

*Siemens AG, Forschungslaboratorien, München, Germany*

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Energy transfer of bound excitons in GaP:N is investigated by time-resolved, resonant-excitation spectroscopy and by studies of below-band-gap excitation spectra. Exciton tunneling is found to dominate over dipole-dipole interactions because of the large spatial extent of the exciton wave function. This is the first definitive observation of exciton tunneling in a semiconductor.

The mechanisms by which localized excitations move through a solid are of interest to various branches of solid state physics. An important example occurs in some laser materials where the dipole-dipole interaction is usually responsible for energy transfer.<sup>1</sup> In III-V semiconductors, "concentration quenching" of shallow bound excitons gives evidence of energy transfer,<sup>2,3</sup> but until now this has not been the subject of full investigation.<sup>4</sup> We show that in GaP:N, transfer can occur over distances an order of magnitude greater than in insulating laser materials. The difference originates from the very large extent of the exciton wave function, which allows tunneling to dominate over the dipole-dipole interaction.

In GaP:N, the isoelectronic impurity nitrogen binds excitons both to the isolated N atom (*A* and *B* excitons) and to near-neighboring nitrogen pairs (NN<sub>i</sub> excitons). A series of about ten dis-

tinct bound-exciton levels may be observed in luminescence and absorption spectra.<sup>2</sup> The N concentrations of our samples were found from the absorption strength of the *A* line, using the calibration of Lightowers, North, and Lorimer<sup>5</sup> and NN pair densities were calculated assuming a random distribution. No evidence for emission originating from any other impurity center was found; thus we conclude the unwanted impurity level to be  $\sim 10^{16}$  cm<sup>-3</sup> or less.

For N concentrations above about  $10^{18}$  cm<sup>-3</sup>, the emission shifts progressively into the lower-energy NN-pair lines. This behavior is clearly seen in published spectra<sup>2</sup> of GaP:N, and examples are shown in Fig. 1 for two samples having N concentrations differing by an order of magnitude. The changing statistical concentration of NN pairs cannot explain this quenching; in the heavier doped sample V59, the NN pairs that dominate the emission (Fig. 1) account for less

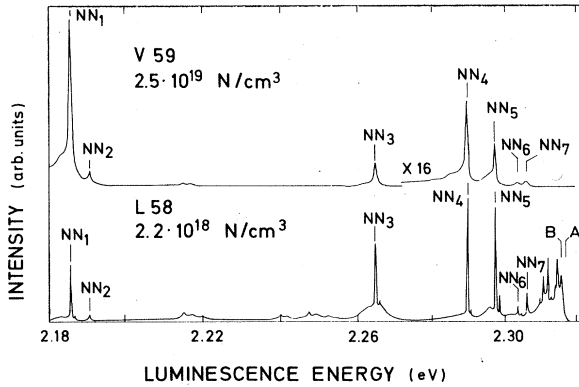


FIG. 1. Luminescence spectra of GaP:N excited by above-band-gap radiation.

than 5% of the total nitrogen content. Furthermore the A line dominates the absorption in all samples. The quenching cannot be explained by reabsorption either. Possibly this has little effect on the A line, but the absorption coefficients at the NN lines are very small compared to that of the excitation light. We conclude that quenching occurs by energy transfer from higher- to lower-energy NN excitons. The transfer must be by direct interaction between neighboring pairs, since we can rule out thermal excitation to the free-exciton level at the temperature of our experiments ( $\sim 1.6$  K). From the observed 80% quenching of NN<sub>3</sub> in samples V59 (Fig. 1), and the calculated total concentration of NN<sub>1</sub> and NN<sub>2</sub> of  $2 \times 10^{17} \text{ cm}^{-3}$ , we estimate that transfer must occur over at least 100 Å, within the radiative lifetime of the exciton ( $\sim 1 \mu\text{sec}$ ). This distance is surprisingly large when compared to typical values of order 10 Å in insulating laser materials.<sup>1</sup>

For a detailed investigation of the energy transfer we use resonant-excitation techniques, employing a tunable dye laser, to isolate specific transitions. The transfer rate was determined from time-resolved measurements using the dye laser with a cavity dumper, which gave light pulses of 15-nsec width and a spectral resolution of 0.3 Å. In Fig. 2 we show below-band-gap excitation spectra of the NN<sub>1</sub> emission. The spectral features can be classified into two types. (1) States associated with the NN<sub>1</sub> exciton, such as phonon side bands and excited states.<sup>6</sup> Here absorption is at the NN<sub>1</sub> site and no spatial transfer occurs. (2) Higher-energy bound excitons, labeled NN<sub>*i*</sub> in Fig. 2. For these to excite NN<sub>1</sub>

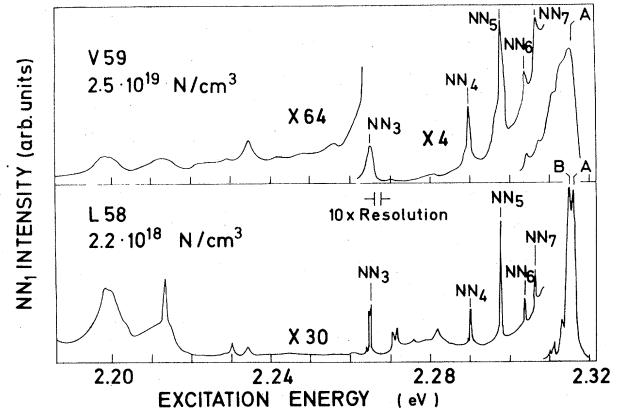


FIG. 2. Excitation spectra of the NN<sub>1</sub> luminescence. Unlabeled structure is mostly from phonon side bands and excited states of NN<sub>1</sub> as reported in Ref. 6.

emission, energy transfer must occur. An unambiguous classification of the peaks in Fig. 2 is possible by investigating the excitation spectra of the different NN lines together with the emission spectra at various excitation energies.<sup>7</sup>

For each sample a series of decay-time measurements were made corresponding to excitation into NN<sub>*i*</sub> and emission from NN<sub>*j*</sub>. When  $i=j$  we refer to this as resonant decay, and if  $i>j$  we refer to it as transfer decay. As an example, Fig. 3 shows the NN<sub>5</sub>–NN<sub>1</sub> transfer decay of sample L58. A build-up of intensity is seen which continues after the end of the laser pulse. There is no such rise with resonant decay, but instead, when transfer is strong, a fast initial

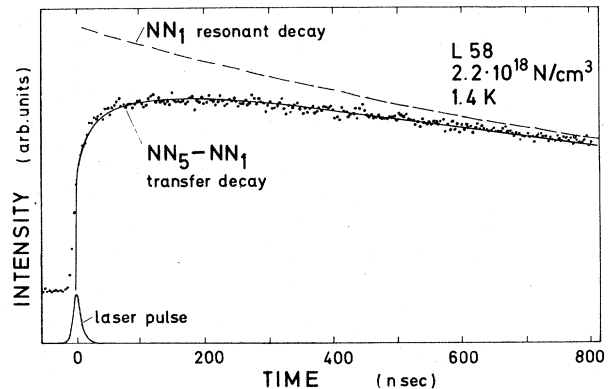


FIG. 3. Time-resolved intensity of NN<sub>1</sub> luminescence for NN<sub>5</sub> excitation. The data are corrected for the small residual transfer effects from phonon side bands of NN<sub>1</sub>. The solid line is a theoretical fit to the data, as described in the text.

decrease of intensity over the same time scale occurs. Both effects originate from the characteristic rate of exciton transfer. The true radiative exciton decay, found from weakly doped samples, is accurately exponential over at least three decades of intensity.

The exciton transfer rate  $P(R)$  will depend on the separation  $R$  of the two exciton sites involved, and thus the spatial distribution  $G_i(R)$  of nearest-neighbor sites has to be considered.<sup>8</sup> For a random distribution and the continuum approximation,

$$G_i(R) = 4\pi R^2 n_i \exp(-4\pi R^3 n_i / 3), \quad (1)$$

where  $n_i$  is the total number of NN pairs to which transfer can occur from  $NN_i$ . Resonant decay will be given by

$$I_i^{\text{res}}(t) = \text{const} \exp(-t/\tau) \times \int_0^\infty G_i(R) \exp[-tP(R)] dR, \quad (2)$$

where  $\tau$  is the true radiative lifetime of  $NN_i$ , and transfer decay by

$$I_i^{\text{tran}}(t) = \text{const} \exp(-t/\tau) \times \int_0^\infty G_i(R) [1 - \exp(-tP(R))] dR. \quad (3)$$

Here we have assumed the radiative lifetimes of both levels to be equal, an approximation borne out by experiment. Derivation of the fraction  $F_i$  of excitons that transfer is also straightforward; if  $P(R)$  is a rapidly changing function of  $R$  then

$$F_i = 1 - \exp(-4\pi R_0^3 n_i / 3), \quad (4)$$

where  $R_0$  is given by  $\tau P(R_0) = 1$ .

The form of the transfer rate  $P(R)$  depends on the interaction Hamiltonian for the transition. For a dipole-dipole interaction,  $P(R)$  varies as  $R^{-6}$ , and the proportionality constant has been calculated by Dexter.<sup>9,1</sup> While a fit to the data of Fig. 3 can be forced with  $P(R) = CR^{-6}$ , the required constant  $C$  is orders of magnitude larger than Dexter's. This is readily apparent from the very large values of  $R$  occurring in the present experiments, an order of magnitude larger than typical situations where dipole-dipole transitions are known to occur. Furthermore the NN exciton emission is principally in the dipole forbidden  $J=2$  component and the weaker quadrupole-dipole interaction would, in fact, be required. Finally the energy difference between levels necessitates a phonon interaction term in the Hamiltonian which would further reduce  $P(R)$ . Interactions based on the radiation field are therefore of insufficient strength to explain the

energy transfer.

An alternative interaction is that of tunneling. The excitons in GaP:N differ from the situation analyzed by Dexter<sup>9</sup> in the large spatial extent of the wave function, due to the relatively small binding energy, making tunneling over considerable distances possible. Furthermore the Hamiltonian for the tunneling transition originates from the phonon interaction,<sup>10</sup> and thus the phonon participation does not need to be considered separately. For tunneling,  $P(R) = \omega_0 \exp(-2R/a_{ij})$ ,<sup>10</sup> where  $\omega_0$  is typically  $10^{12} - 10^{13} \text{ sec}^{-1}$ .  $a_{ij}$  is an effective exciton radius, a combination of the radii of the initial and final states, which also must take into account any exciton anisotropy.<sup>10</sup>

Using the tunneling expression for  $P(R)$ , Eqs. (2), (3), and (4) may be expressed in terms of a parameter  $q = a_{ij} n_i^{1/3}$ . The value of  $a_{ij}$  is not precisely calculable for the NN lines and therefore  $q$  is taken as a variable to be determined. An accurate fit of Eq. (3) to the transfer data is obtained as shown in Fig. 3, where we have taken  $\omega_0 = 10^{13} \text{ sec}^{-1}$ . If  $\omega_0$  is reduced to  $10^{12} \text{ sec}^{-1}$ ,  $q$  increases by about 25%, indicating the relative insensitivity of  $q$  to the exact values of  $\omega_0$ . Using the value of  $q$  deduced from this analysis of  $I_i^{\text{tran}}(t)$ , acceptable fits to the data (not shown) for both  $I_i^{\text{res}}(t)$  and  $F_i$  have also been obtained, indicating the consistency of the model. Calculating  $n_i$  from the total nitrogen concentration, we find  $a_{ij} \approx 40 \text{ \AA}$ . Until the  $NN_i$  concentrations can be obtained directly rather than by calculation, the inferred  $a_{ij}$  remains only approximate. However the magnitude of this value is clearly reasonable, although no reliable calculation of the exciton radius exists to allow detailed comparison.

In conclusion dipole-dipole and similar interactions based on the radiation field are found unable to explain the large transfer distances. On the other hand, the tunneling hypothesis fits the data with physically reasonable parameters. The large extent of the shallow exciton wave functions is the reason for the predominance of tunneling.

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Planck-Institut für Festkörperforschung, Stuttgart, Germany.

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## Chemical-Bond Approach to the Magnetic Susceptibility of Tetrahedral Semiconductors\*

V. P. Sukhatme† and P. A. Wolff

*Center for Materials Science and Engineering and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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A chemical-bond theory of the magnetic susceptibility of tetrahedral semiconductors is presented. Starting from a Hall-Weaire-type Hamiltonian, we derive an expression for the susceptibility, whose diamagnetic and paramagnetic contributions are written in terms of gauge-invariant physical quantities. Our analysis confirms a recently postulated model for the susceptibility. Theory and experiment are in good agreement.

In a recent Letter,<sup>1</sup> Hudgens, Kastner, and Fritzsche (HKF) proposed a model susceptibility function for tetrahedral semiconductors of the form

$$\chi = \frac{-N_0 e^2}{6mc^2} \left[ \sum_{\text{core}} \langle r^2 \rangle + \sum_{\text{val}} \langle r^2 \rangle \right] + \frac{|M|^2}{E_g}. \quad (1)$$

They ascribed the first two diamagnetic terms in this formula, denoted by  $\chi_c$  and  $\chi_v$ , to core and valence electrons, respectively; the last term ( $\chi_p$ ) is a Van Vleck paramagnetic susceptibility arising from virtual interband transitions. HKF also measured the susceptibility, and its temperature dependence, for diamond, Si, Ge, GaAs, and GaP. From these data, they could then *separately* determine  $\chi_v$  and  $\chi_p$ . They find nearly complete cancelation between  $\chi_v$  and  $\chi_p$ , a constant interband matrix element ( $|M|^2$ ) despite wide variations in  $E_g$ , and values of  $\langle r^2 \rangle_{\text{val}}^{1/2}$  that scale with lattice spacing. These results support their model, but leave several questions unanswered. In particular, the meaning of the various terms ( $\langle r^2 \rangle_{\text{val}}$ ,  $|M|^2$ , etc.) appearing in Eq. (1) remains unclear. It is not obvious, moreover, that such quantities are gauge invariant. The purpose of

this Letter is to sketch a derivation of the HKF model which resolves these difficulties. We will show that Eq. (1) follows from a simple tight-binding picture, and we will present explicit expressions for the various terms in this formula, which do not depend on the choice of origin of the vector potential. The values of  $\langle r^2 \rangle_{\text{val}}$  and  $|M|^2$  calculated from these expressions agree with those measured by HKF. These quantities have a chemical significance, and can be used (as HKF suggest) to characterize bonding in tetrahedral semiconductors. In this sense, the theory developed here is similar to recently proposed dielectric theories of chemical bonding.<sup>2,3</sup> On the other hand, our work is complementary to that of previous authors,<sup>4</sup> who have derived exact, but complicated, expressions for the magnetic susceptibility of crystals.

The Hall-Weaire (HW) model<sup>5,6</sup> is the starting point for our description of the magnetic properties of tetrahedrally bonded solids. This model has often been used to discuss the electronic structure of diamond-type semiconductors<sup>5-7</sup>. It is also the basis for one of the dielectric theories of bonding mentioned above.<sup>3</sup> To incorporate the effects of a magnetic field into the HW model, we introduce a basis set of gauge-invariant,  $sp^3$ ,