465 (1965).

[2] H. Bizette, C. Terrier, and B. Tsai, Compt. Rend. 243, 895 (1956).

[3] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Phys. Rev. 113, 497 (1959).

[4] I. S. Jacobs, S. Roberts, and P. E. Lawrence, General Electric Research Laboratory Report No. 64-RL-3847M, December 1964; J. Appl. Phys. Suppl. 36, 1197 (1965).

[5] O. Trapeznikowa and L. Schubnikow, Phys. Z. Sowietunion 7, 66 (1935).

[6] J. Kanamori, J. Phys. Chem. Solids 10, 87 (1959).

[7] T. Wolfram and J. Callaway, Phys. Rev. 130, 2207 (1963).

[8] S. Takeno, Progr. Theoret. Phys. (Kyoto) 30, 731 (1963).

[9] Li Yin-Yuan and Zhu Yan-Qing, Acta Phys. Sinica 19, 753 (1963).

[10] H. Ishii, J. Kanamori, and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 33, 795 (1965).

ISOELECTRONIC TRAPS DUE TO NITROGEN IN GALLIUM PHOSPHIDE

D. G. Thomas
Bell Telephone Laboratories, Murray Hill, New Jersey

and

J. J. Hopfield
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey

and

C. J. Frosch
Bell Telephone Laboratories, Murray Hill, New Jersey

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It is generally assumed that an isoelectronic substitution of a lattice atom in a semiconductor produces no bound states within the forbidden band gap. This paper shows that many such states arise from the substitution of nitrogen for phosphorus in GaP.

An optical transition, called *A-B*, which has previously not been understood, is frequently seen in the low-temperature fluorescent and absorption spectra of gallium phosphide. This transition has been shown[1] magnetically to involve a nondegenerate ground state and an electron-hole pair in the excited state, but the binding energy of the exciton to the center is an order of magnitude too low to correspond to an exciton bound to a charged impurity. Evidence is presented here that this transition is due to isolated nitrogen on phosphorus sites and that a series of lines (variously labelled *D*, *E*, *F*, *G*, *H*,[1] and as a converging series[2]), visible in emission and absorption, are due to nitrogen-nitrogen pairs.

Absorption, unlike fluorescence, provides a direct measure of the *A-B* center concentration. Many strongly fluorescent crystals were found to have weak *A-B* absorption, but a dramatic increase in this absorption occurred for crystals that were grown by a modified water-transport method[3] in boron nitride vessels at about 1000°C. These crystals are red in transmitted light at room temperature due to the strong *A*-center absorption; pure crystals are orange. The red crystals have very low conductivities at 300°K indicating an electrically inactive impurity. A low-temperature absorption spectrum is shown in Fig. 1(a). If quartz vessels were used, or quartz vessels and boron, orange crystals resulted. It was therefore suspected that nitrogen caused the *A*-line absorption. Since nitrogen gas was found to produce only weak effects, it appeared that the active source of nitrogen was NH_3 made by the high-temperature reaction of H_2O with BN. Red crystals may also be grown from Ga solution, readily in the presence of small quantitites of NH_3, but only at hazardously high pressures in the presence of pure N_2 (derived from GaN).

The spectrum associated with NN pairs consists of a series of lines, each a fine-structure multiplet, observable in the energy range from a few to 132 meV below the *A-B* transition. These lines are shown in absorption in Fig. 1(a) and in fluorescence in Fig. 1(b). They are labeled NN_1, NN_2, etc. They form a series which decreases in energy separation toward shorter wavelengths. Gross and Nedzvetskii sug-

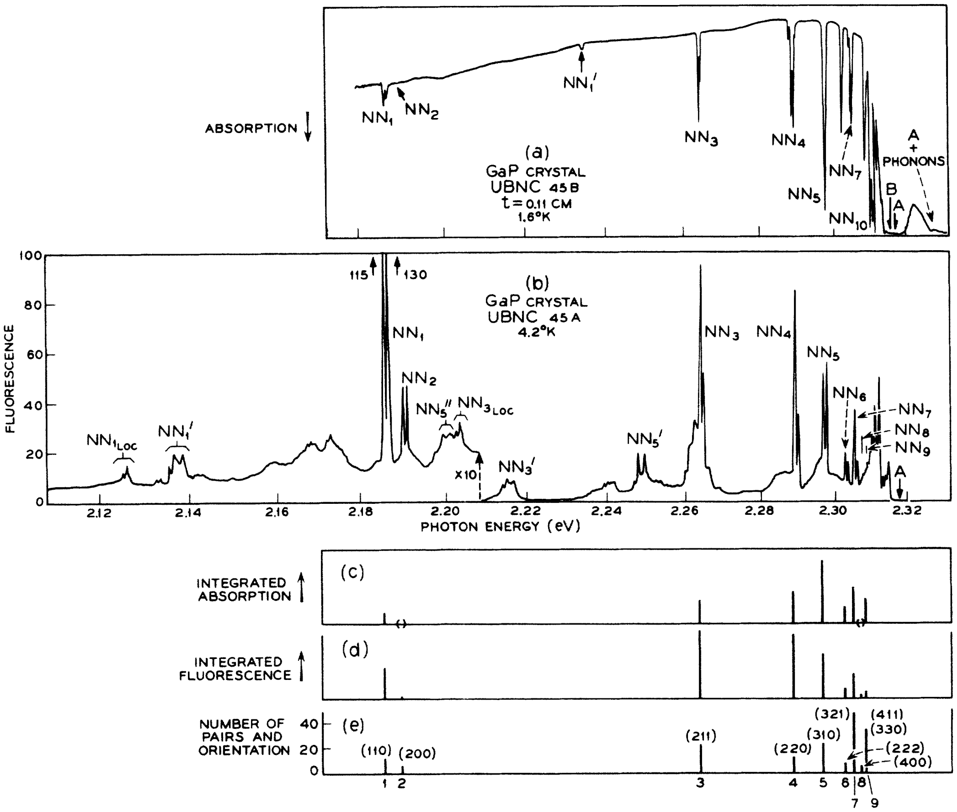

FIG. 1. The NN lines (a) in absorption and (b) in fluorescence in crystals containing about 10^{19} N atoms/cc. Lattice phonon replicas have been labelled NN_5', NN_5'', etc. Local modes are labelled NN_{1loc}, etc. In more lightly doped crystals there is a sharp *A* line in absorption and fluorescence; here the *A* line (and its higher energy phonon wings) dominates the absorption, but is very weak in emission. (c) and (d) show the approximate relative strengths of the lines in absorption and fluorescence. (e) shows the expected relative intensities of the lines if it is assumed that the nitrogen atoms are arranged randomly and that relative numbers alone control the transition intensities. The orientations of the pairs are also indicated.

gested[2] that these fluorescent lines were due to transitions which originated at an exciton bound to an acceptor in its ground state, and which terminated on an excited state of the acceptor. The fact that lines many millivolts apart are visible in absorption at 1.6°K shows that this cannot be the case. In addition, this model would predict that the lines converge towards lower energies, whereas, in fact, Fig. 1 shows that they converge towards higher energies.

In Fig. 1(b) the NN pairs are seen in fluorescence at 4.2°, yet the *A* line is absent or very weak despite the fact that it is very strong in absorption. This is because at these high nitrogen concentrations an exciton bound to *A* may readily transfer to an NN-pair state which has a lower energy. This situation represents incipient impurity banding of the bound excitons. At lower concentrations *A* becomes apparent in fluorescence and at very low concentrations (e.g., 10^{16} atoms/cc), it, and its phonon wings, dominate the emission.

A-B shows only a *jj*-coupling–induced splitting, any cubic-field splitting of the $J=2$ state into a doublet being too small to observe. This is consistent with a simple point defect and hence an isolated N atom. Many of the NN-pair lines, however, show complex structure; for instance, NN_1 has six components, three from the $J=1$ line and three from the $J=2$ (this detail is not visible in Fig. 1). Such splittings could arise from lowered symmetry if the center consisted of two foreign atoms. If it is assumed that the N atoms, being uncharged, are distributed randomly, then the small concentration of pairs of N atoms is expected to vary as the square of the total nitrogen concentration. The absorption of the *A* line (or more conveniently its phonon wing), and of the NN lines (in particular NN_{10}), have been measured in a series of differently doped crystals of variour thicknesses. Figure 2 shows that the NN_{10} absorption varies as the square of the *A*-line absorption and confirms that the NN lines arise from pairs of nitrogen atoms. Further confirmation comes from the Zeeman pattern of the NN lines. These patterns appear to be based on that of *A*-*B* but show additional structure and marked changes with change of direction of the magnetic field. Frequently, more than eight lines can be resolved, and this can only be accounted for if it is assumed that pairs with different orientations to the field, but of the same separation, give different Zeeman patterns.

The different NN lines correspond to different separations of the N atoms. The exciton must be bound to an isolated nitrogen atom in the same way as a particle is bound to a short-range potential well. If the well is made deeper by placing two nitrogens close together the binding can become much tighter. As the NN separations become large the differences in energy positions of the corresponding lines must become less. Since the lines converge at higher energies (where line identification ultimately becomes difficult because the fine structure becomes greater than the main separation), it follows that the higher the energy the greater the spatial separation. An exciton at an isolated N atom is the *A*-*B* state. Hence, the NN lines converge on *A*-*B*. It is reasonable to suppose that the lowest energy line NN_1 corresponds to two N atoms on nearest-neighbor phosphorus sites; NN_2 to a pair on the next-nearest neighbors; and so on. The directions of these pairs and their relative numbers, assuming a random distribution, are known from the lattice geometry, and are shown in Fig. 1(e). The relative intensities of the lines in absorption and emission shown in Fig. 1(c) and 1(d) provide qualitative confirmation of this assignment. Notice that NN_2, NN_6, and NN_8 are expected and observed to be weak. The fine structure of the lines also provides circumstantial support. Thus, the local symmetry around pairs with [111] or [100] orientations cannot split the $J=1$ state into a triplet, but a [110] orientation, for example, can. NN_2, NN_6, and NN_8 are of the former class and have singlet or doublet $J=1$ states, whereas NN_1 has [110] orientation and its $J=1$ state is a triplet. It is interesting to notice that unless both members of the pairs were the same, certain pairs, such as those in [111] directions, would have inequivalent orientations, viz. [111] and $[\bar{1}\bar{1}\bar{1}]$. The absence of any abnormal fine structure for these pairs is further evidence that two nitrogen atoms are involved in the states.

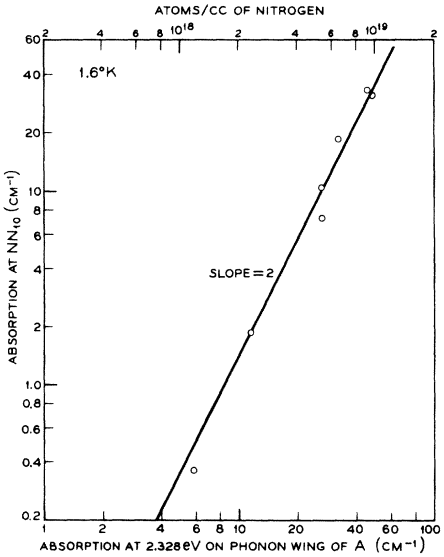

FIG. 2. The absorption of line NN_{10} plotted against the absorption in the phonon wing of the *A*-*B* lines, which is proportional to the *A*-*B* center concentration. Each point represents a crystal with a different nitrogen doping. The line is drawn with a slope of 2 and shows that the concentration of the NN centers varies as the square of the concentration of the *A*-*B* center. The concentration scale is obtained as indicated in the text.

The concentration of the nitrogen present may be estimated by purely optical methods if a random distribution and a constant matrix element for the transitions are assumed. It is then apparent that

$$\frac{\text{Strength of NN}_m\text{ in absorption}}{\text{Strength of }A\text{ in absorption}}=\frac{N_m}{2}\frac{N}{N_0},$$

where N_m is the number of *P* atoms in the *m*th shell (24 for NN_{10}), *N* is the concentration of "isolated" nitrogen (which is much larger than the concentration of the pairs), and N_0 is the number of P sites/cc of GaP. Using NN_{10} the concentration scale shown on Fig. 2 was derived. The measurement of extremely sharp lines, and pair-geometry-dependent matrix elements limit the accuracy of the concentration calibration to an estimated factor of five.

The first suggestion that nitrogen was involved in the centers was actually obtained from the fluorescent phonon wings of the more tightly bound NN lines. All the lines display phonon wings corresponding to lattice phonons, but the deep lines give distinct phonon replicas which correspond to energies greater than that of the LO lattice phonon. These must represent local modes and have been labeled in Fig. 1 for NN_1 and NN_3. It is found that $\hbar\omega_{loc} = 0.061$ eV. If $\hbar\bar{\omega}$ (=0.048 eV) is the average of the lattice TO and LO phonons,[1] a crude model gives for the local mode frequency

$$\omega_{loc} \approx \bar{\omega}\left\{\frac{1/4M_{Ga} + 1/M_{N}}{1/M_{Ga} + 1/M_{P}}\right\}^{1/2} = 1.27\bar{\omega},$$

where M_N is the atomic weight of nitrogen, etc. Experimentally, $\omega_{loc} = 1.27\bar{\omega}$ in coincidentally good agreement with the expected value. The local modes are more important for the deeper bound excitons because these more tightly bound states have wave functions more concentrated at the central nitrogen atoms.

Several other series of lines have been observed which are generically related to the NN lines, and which probably involve elements other than nitrogen. This type of binding to neutral centers may therefore be quite common and may lead to a wide variety of states within the forbidden gap of semiconductors. It seems likely that at least some of these centers will bind not only excitons but also either holes or electrons. They may therefore influence not only optical but also electrical properties of semiconductors.

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[1] D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. 131, 2397 (1963).

[2] E. F. Gross and D. S. Nedzvetskii, Dokl. Akad. Nauk SSSR 154, 64 (1964) [translation: Soviet Phys.—Doklady 9, 38 (1964)].

[3] C. J. Frosch, J. Electrochem. Soc. 111, 180 (1964).

SUPERCONDUCTIVITY OF PROTACTINIUM*

R. D. Fowler, B. T. Matthias, L. B. Asprey, H. H. Hill
J. D. G. Lindsay, C. E. Olsen, and R. W. White

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico

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We have observed superconductivity in protactinium metal below 1.4°K and thus filled the last vacant spot in the center of the periodic system, the region in which every element becomes either superconducting, ferromagnetic, or antiferromagnetic. We show in the following table the position of Pa in relation to its surrounding elements with their superconducting transition temperatures.

Hf 0.1	Ta 4.4	W 0.011
Th 1.4	Pa 1.4	U 0.7(o), 1.8(c)[a]

[a] The two polymorphic modifications of uranium are orthorhombic and cubic. They have different transition temperatures. See B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem. Solids 7, 259 (1958).

Pa has five valence electrons and hence would be expected to have the highest transition temperature in the series Th, Pa, U. All surrounding elements are superconductors, and by analogy with the Hf, Ta, W series, Pa would be expected to have a very high transition temperature, certainly far above 18°K. This reasoning would hold, however, only if Pa were to crystallize in one of the simple elemental structures. It is therefore of interest that Zachariasen found an entirely different crystal structure for Pa,[1] namely, that it is tetragonal with a tenfold coordination, a structure observed to date only for Pa. The fact that Pa metal has a more complicated structure than most metals is in agreement with the empirical observation that, whenever a metal could be expected to have a very high transition temperature, it was found instead to have a lower crystal symmetry and therefore also a lower transition temperature.

While these arguments, based on analogies to superconductors in other parts of the peri-