

Theory of Metallic Diamond*†

W. F. LIBBY

Department of Chemistry and Institute of Geophysics, University of California, Los Angeles

(Received 5 December 1962)

The fact that compression of Group IV elements and of Groups III-V and II-VI binary compounds forms new denser phases with six near neighbor body-centered tetragonal lattices which are metallic requires theoretical explanation. We think of this new set of metals as being typified by the expected new metallic phase of carbon to be obtained by compression of diamond which we call metallic diamond. It is proposed that this new class of metals of which tin is the only present example under ordinary conditions, and which may include a new metallic form of carbon denser than diamond called metallic diamond, can be understood as a three-dimensional analog of the two-dimensional metal graphite. The excess number of geometrically equivalent nearest neighbors over the four bonds possible from the available electrons and orbitals causes crystal-wide resonance which gives the metallic properties.

I. INTRODUCTION

IT is known now¹⁻³ that the compression of Group IV elements and of the III-V or II-IV binary compounds transforms them into metals. The phase change is marked by a large increase in density and a rise in the number of equivalent near neighbors from four characteristic of these materials at low pressure to six in the new phase.⁴ The generality of this phenomenon indicates that a previously unrecognized principle must be involved, and it is the purpose of this paper to suggest a general theory for this transformation.

II. THEORY

The eight electrons available for bonding in the low-pressure tetrahedral structures just fill the four available orbitals and at the same time establish equivalent bonds to all near neighbors. It is our theory that the forced transformation to a more densely packed structure with more than four neighbors without any increase in the number of bonding electrons or available orbitals causes the system to become metallic.

Why should this be so? For ordinary metals, vacant orbitals exist from which conducting bands readily form. Can it be that this is not the only type of metallic conduction, or do we in making the new metals discussed here so transform the energy levels in the compression act itself that higher orbitals become available? An-

other possibility is the Pauling⁵ theory for tin (tin is the only member of the new class of metals which is stable under ordinary conditions). Pauling says that 1.44 of the 4 valence electrons on the average are set aside from the bonding function to form 0.72 nonbonding pair and that this creates 0.72 orbital vacancy and leaves 2.56 valence electrons for bonding.

It is our suggestion that it is not necessary to have vacant orbitals but that metallic conduction can result purely from the resonance condition that must exist in a structure which has more truly geometrically equivalent near neighbors than there are possible bonds. Of course, at very high compressions all matter will become metallic⁶⁻⁸ since all electron levels are raised by compression and the ionization potential thus must fall to zero eventually, but before this occurs the new class of resonating metals will occur because the degree of compression necessary to the raising of the coordination number above the bond number probably is less than that for enforced ionization.

Our theory can be illustrated in many ways, but the central point is that the condition of geometrical equivalence means that the Franck-Condon principle offers no barrier to electronic resonance with the consequence that resonance occurs throughout the region of geometrical equivalence which may be crystal wide.

Every resonating system can be thought of either in terms of band theory or in terms of alternative dispositions of bonds which are equally likely. In the band theory, for our case of four orbitals and four valence electrons, one sees immediately that the $4N$ electrons of the N equivalent atoms in the macroscopic crystal will lie in the bottom half of the $4N$ levels made by combining the $4N$ orbitals in resonance; and the whole question then becomes one as to whether the splitting of the $4N$ levels is such as to create a gap between the bottom and top sets of $2N$ levels and thus to prevent

* Publication No. 267, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.

† This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under the Contract No. AF 49(638)-901.

¹ A. Jayaraman, R. C. Newton, and G. C. Kennedy, *Nature*, **191**, 1288 (1961); "High Pressure Studies on Diamond and Zinc Blende Structures: Melting and Polymorphism," presented at the Diamond Symposium in Paris, May 1962 (unpublished); A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **129**, 540 (1963).

² B. J. Alder and R. H. Christian, *Phys. Rev. Letters* **8**, 367 (1961).

³ H. L. Suchan and H. G. Drickamer, *J. Chem. Phys.* **31**, 355 (1959); S. Mimomura and H. G. Drickamer, *J. Phys. Chem. Solids* **23**, 451 (1962); G. A. Samara and H. G. Drickamer, *ibid.* **23**, 457 (1962); *J. Chem. Phys.* **37**, 408 (1962).

⁴ J. C. Jamieson, *Abstracts for 1962* (Geological Society of America, New York, 1963), Special Paper 73, p. 178.

⁵ L. C. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.

⁶ E. Wigner and H. B. Huntington, *J. Chem. Phys.* **3**, 764 (1935).

⁷ C. A. ten Seldam, *Proc. Phys. Soc. (London)* **A70**, 97, 529 (1957).

⁸ R. E. Behringer, *Phys. Rev.* **113**, 787 (1959).

ready promotion to the conducting levels above the top Fermi level in the ground state. In graphite, which is the two-dimensional case for our system, there are one orbital and one valence electron per atom with three equivalent neighbors. For graphite it is clear both theoretically⁹ and experimentally^{7,10} that the two-dimensional metallic state exists. Thus, we see that for this system, at least, *bond resonance without vacant orbitals can produce the metallic state*. It is our theory that the new class of metals discussed here is the three-dimensional analog of the two-dimensional metal graphite. There are four orbitals and four valence electrons with four neighbors in the tetrahedral lattices of diamond, wurtzite, and sphalerite which on compression transform, according to Jamieson,⁴ into the six-near-neighbor structure of metallic tin. Thus four bonds have to satisfy six atoms (the central atom contributes 4 valence electrons and each of the surrounding 6 atoms contributes 4/6 more for a total of 8, just adequate for four full bonds). The resonance state is possible because the Franck-Condon principle has been satisfied by the location of the atoms in equivalent positions, and, as a consequence, the full crystal is set into three-dimensional resonance such that the entire crystal becomes one molecule at least at the absolute zero of temperature. At finite temperatures the

principle of strict symmetrical equivalence for neighbors will be violated by the lattice vibrations, and the resonance possibilities will be reduced because of the Franck-Condon principle; or in band theory language the scattering of conducting electrons will result.

The conduction act itself can be most clearly envisaged as the removal of an electron from the resonating molecule at one edge of the crystal at the cost of the ionization potential, the distribution of the resultant positive charge uniformly over the entire molecule because of the three-dimensional resonance, followed by the neutralization by acquisition of an electron at the opposite side of the crystal with the regaining of the energy corresponding to the ionization potential. In the presence of an electric field the positive charge obviously will not be completely uniformly distributed at any finite temperature because the relaxation time for the molecular lattice will necessarily be the time for the transport act in order that the charge be passed from anode to cathode, and this limitation in rate will cause a charge gradient to exist across the molecule. At the absolute zero of temperature this electrical resistance would appear to be zero.

Drickamer³ and his co-workers have shown that, like true metals, the new compressed phases absorb light down to the lowest frequencies. This can be envisaged as being due to the close lying states in the crystal (molecule) corresponding to charge displacement from one end of the crystal to the other.

⁹ P. R. Wallace, Phys. Rev. **71**, 622 (1947).

¹⁰ A. R. Ubbelohde and F. A. Lewis, *Graphite and Its Crystal Compounds* (Clarendon Press, Oxford, 1960).

Optical Absorption in an Electric Field

JOSEPH CALLAWAY*

Aeronutronic Division of Ford Motor Company, Newport Beach, California

(Received 3 December 1962)

The effect of an external electric field on the optical absorption associated with a direct transition between bands is studied. Expressions are given for the absorption constant for photon energies below and above the band gap. The formation of discrete levels in the presence of the electric field produces oscillations in the absorption.

THE influence of an electric field on the optical absorption of a semiconductor or insulator in the vicinity of an absorption edge has previously been studied by Franz¹ and by Keldysh.² These authors have shown that in the presence of a field, absorption occurs for photon energies lower than the ordinary band gap. This effect has been observed experimentally by Moss,³ Williams,⁴ Böer *et al.*,⁵ and Vavilov and

Britsyn.⁶ In addition to the displacement of the edge, one expects to find oscillatory behavior of the absorption above the edge resulting from transitions between the discrete "Stark" levels produced in the band system by the external field.⁷ This structure might be similar to that observed in the interband magneto-optical effect by Burstein *et al.*⁸ and by Zwerdling *et al.*⁹ The

* Consultant. Permanent address: Department of Physics, University of California, Riverside, California.

¹ W. Franz, Z. Naturforsch. **13**, 484 (1958).

² L. V. Keldysh, Soviet Phys.—JETP **7**, 788 (1958).

³ T. S. Moss, J. Appl. Phys. **32**, 2136 (1962).

⁴ R. Williams, Phys. Rev. **117**, 1487 (1960); **126**, 442 (1962).

⁵ K. W. Böer, H. J. Hänsche, and U. Kummel, Z. Physik **155**, 170 (1959).

⁶ V. S. Vavilov and K. I. Britsyn, Soviet Phys.—Solid State **2**, 1746 (1961); L. V. Keldysh, V. S. Vavilov, and K. I. Britsyn, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague 1961), p. 824.

⁷ G. Wannier, Phys. Rev. **117**, 432 (1960).

⁸ E. Burstein, G. S. Picus, R. F. Wallis, and F. Blatt, Phys. Rev. **112**, 15 (1959).

⁹ S. Zwerdling, B. Lax, L. M. Roth, and K. J. Button, Phys. Rev. **114**, 80 (1959).