

White tin can be kept at temperatures below the temperature at which gray is the stable form ( $13^{\circ}\text{C}$ ),<sup>8</sup> if it is free of nucleation centers. White tin, even in the presence of nucleation centers can be kept in the metastable state for long periods of time if the temperature is kept sufficiently low ( $-196^{\circ}\text{C}$ ).

The technique then is to carry out the transformation from the nonmetallic to the metallic phase, to cook the metallic phase by prolonged heating and compression to rid it of nonmetallic nuclei, then to cool the entire apparatus with liquid nitrogen down to  $-196^{\circ}\text{C}$  at which point the pressure is reduced to 1 atm and the sample removed from the apparatus under liquid nitrogen. In those cases in which it is possible to attain sufficiently high pressures and temperatures to obtain the metallic phase directly from the melt, the cooking step is unnecessary and there is little problem in obtaining a solid free of nuclei of the original phase.

The solid-solid transformation, however, can be carried out directly in those cases where it is impossible to melt or very difficult to melt under high pressure by the cooking technique using pressures in excess of equilibrium pressure for many hours to affect a complete conversion of the sample. It appears to be helpful to change the pressure and temperature in a somewhat random and arbitrary manner to effect a kind of cruising in the metallic field of the phase diagram.

The metastable materials obtained so far have been found to differ widely in the temperatures to which they can be warmed before they transform back to the normal low-pressure phase. The technique has been applied previously to ice.<sup>9</sup>

### III. THE THEORY OF METALLIC DIAMOND

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.<sup>10</sup> 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.

We suggest that it is not necessary to have vacant orbitals for the metallic state<sup>11</sup> 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 metallic<sup>12-14</sup> 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.

The 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 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 theoretically<sup>15</sup> and experimentally<sup>16</sup> 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 metals produced here are the three-dimensional analogs of the two-dimensional metal graphite and that tin itself is such a case (we call these metallic diamonds as a class name). There are four orbitals and four valence electrons with four neighbors in the tetrahedral lattices of diamond, wurzite, and sphalerite which on compression transform, according to Jamieson,<sup>17</sup> into the six-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

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<sup>17</sup> J. C. Jamieson, *Abstracts for 1962* (Geological Society of America, New York, 1963), Special Paper 73, p. 178.