

noted that sensitizers need not always be absolutely photostable since energy transfer to the substrate, reaction 3, will often reduce the photoreactivity of the sensitizer. Many carbonyl compounds undergo photo-reduction in solvents that serve as hydrogen donors.^{19,20} For this reason we have often chosen to carry out sensi-

(19) A. Schönberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

(20) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).

tized reactions in benzene, a poor hydrogen donor. *Triphenylene* is recommended as an especially good sensitizer for orienting experiments since it absorbs at relatively long wave lengths (ϵ 100 at 3450 Å.), undergoes intersystem crossing with high efficiency (95%), gives triplets with relatively high excitation energy (\sim 67 kcal.), and is exceptionally photostable.

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Formation of Diamond. III. Effects of Silicon on the Nucleation and Growth of Diamond. Comparison of Effects with Other Light Atom Impurities

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The effects of silicon on the catalyzed diamond-forming reaction have been studied and are found to depend on the form and purity of the Si compound used to dope the reaction mix. Oxidation yielding SiO₂ or dissolution of Si in the catalyst metal took place at diamond-stable, high-pressure, high-temperature conditions. Diamond is found intergranularly in a coesite matrix, in the first case, if a suitable excess of carbon is present. In the second case, some diamond is found with N-containing SiC in a Ni-Si acid-resistant matrix. Decomposable compounds of silicon, like CaSi₂, reduce diamond nucleation, slow growth, and promote the formation of rotation twins of diamond on (111). The crystals have very smooth (111) faces, and appreciable amounts of Ni and CaO may be demonstrated to be present in some of these diamonds. The quantitative effect of Si upon nucleation and growth is not so pronounced as that of either boron or aluminum, and it is thus not possible to say that Si is a cocatalyst for diamond formation when employed in conjunction with, *e.g.*, nickel. Strong qualitative effects of these various impurities upon diamond-crystal color are observed, and these are discussed in the Appendix.

Introduction

It was previously observed¹ that the presence of silicon had an unusual effect on the nucleation of diamond in the Ni-Al-C system. Silicon also appears to be involved in the formation of natural diamond. In crystals from the Congo, silicon is widely supposed to cause the tough opaque character of the outer layer. Custers² questioned this supposition; he examined the opalescent skin of such stones and found no evidence of any solid material other than diamond carbon to be present, beyond a few small unknown inclusions. The origin of the supposition may lie in the approximate petrographic similarity between opaque, layered diamond and some forms of silica-like agate, but the matter is not that simple, since we have obtained an analysis of 0.13% Si contained in Congo diamond. It would seem that the best statement is that the opalescent character is not necessarily dependent on Si. That small but measurable amounts of silicon are in fact present in natural diamond has also been demonstrated by spectrographic and neutron activation analysis.³ The presence of silicon must, of course, reflect the nature of the matrix from which the crystals were formed. Silicon might be expected to influence the solubility of carbon in the matrix, and generally to impede diffusion through the bulk of the medium involved, by occupying, *e.g.*, interstitial sites in a metal, thus altering the pattern of nucleation-growth events, as well as the final

product. Again, at all temperatures up to \sim 1850°K., SiO₂ has a higher free energy of formation than does CO, and so Si might serve as a preferred sink for oxygen. If these considerations are significant in the nucleation of diamond, experimental verification should be possible.

It is also important to know, as far as general questions of reaction mechanism are concerned, whether the enhanced diamond nucleation characteristics described earlier¹ are due to a modification of catalyst function or to the action of the impurities as heterogeneous nucleating sites. The problem is complex; prior information shows that many impurities introduced in elemental form do alloy with nickel and that they are actually incorporated into the growing diamond. No clear evidence exists that the inclusions in laboratory-prepared diamond are in general heterogeneous-growth nuclei, and in those cases where noncarbon material has been specifically identified, it seems to be randomly distributed with respect to the cubic axes of diamond. In this connection, carbide needles may be observed in diamond prepared using a Ni-Cr catalyst, but no obvious mutual orientation is apparent. The formation of solid chromium carbide and diamond seems to have taken place simultaneously and very rapidly. Again, the color associated with boron incorporated by growth into diamond is frequently nonuniform. However, in both these latter cases the impurities were alloyed with the nickel in advance of the reaction and thus probably existed as a dilute second phase in the main nickel phase in the solid or solidifying state and as a simple dilute solution in the liquid state. As a consequence it might seem very reasonable that the second component of the catalyst would be bound to appear in the final product,

(1) P. Cannon and E. T. Conlin, 5th International Congress on the Reactivity of Solids, Munich, 1964; see also General Electric Research Laboratory Report RL-3461-C.

(2) J. F. H. Custers, *Am. Mineralogist*, **35**, 51 (1950).

(3) (a) F. G. Freedman, *J. Chem. Phys.*, **26**, 347 (1952); (b) F. G. Chesley, *Am. Mineralogist*, **27**, 23 (1942); (c) F. A. Raal, *Proc. Phys. Soc.*, **71**, 846 (1958).

even if it were not important to the diamond-forming reaction. Thus, it appeared necessary to do experiments using impurities in a high-temperature-stable compound form to give them the best chance to act as heterogeneous nuclei for diamond growth.

Consequently, experiments were done with various silicon-containing impurities, and a comparison was made of the effects of B, Al, and Si on the diamond-forming reaction.

Experimental

(A) (i) **Experiments Involving SiC.**—Even in the presence of nickel, attempts to form diamond from impure silicon carbide ("4F Carborundum") alone met with no success in the range of conditions 55–65 kbars, 1400–1600°. Substantial experimental difficulties arose in attempting to handle such an incompressible material in the Belt apparatus. In experiments in which an excess of carbon was supplied as graphite, however, diamond was formed at these conditions in the presence of SiC, as well as in those cases when a small amount of silicon was added directly to a Ni-C mix. In general, these latter experiments resulted in the formation of a diamond-coesite matrix, with the diamond occupying the spaces between the coesite grains. These effects depend in part on the purity of the SiC used. Thus, some clear, colorless, hexagonal SiC was obtained through the kindness of Dr. G. A. Slack, of this laboratory. This material contains an unusually low amount of nitrogen ($<10^{18}$ N atoms/cc.) and no iron. It was mixed with spectroscopically pure nickel powder and graphite powder. Experiments in the above pressure-temperature range yielded considerable amounts of diamond. Those samples which had contained N-free (colorless) SiC were now found to consist of an acid-resistant metallic core containing N-contaminated (blue) SiC and diamond, together with the tough matrix.

(ii) **Experiments Involving CaSi₂.**—Ni-C and Ni-Al-C powder mixes (2:1 and 2:1:2, atomic, respectively) were doped with 5 wt. % of finely crushed CaSi₂ and then maintained for 20 min. at ~1570° and 55 kbars. Control runs were made without calcium silicide. The diamonds from the NiAlC-CaSi₂ mix were either colorless or black; a few "piebald" stones were also observable. The habit of these stones was good and their 111 surfaces beautifully smooth. The runs with Ni-C-CaSi₂ mixes yielded small amounts (~10 mg.) of excellent crystals of a canary yellow ("cape") color. In all these runs, large amounts of silica were found in the reaction cell. The over-all yields from systems lean in carbon were found to be readily increased by providing a substantial excess of carbon over that required for the formation of Ni₃C + Al₄C₃ + CaC₂ + SiC.

CaSi₂ was then studied as a controlled-level impurity in diamond synthesis. In view of the fact that calcium silicides are believed to stabilize the compound Ni₃C,⁴ it was thought that some definite effects on yield, as well as on habit, might be seen.

All combinations of the conditions presented in Table I were run. The center point of the design was run in quadruplicate, and all other combinations were run once. The 20 runs were

TABLE I

Variable level	Temp., °C.	Pressure, kbars	CaSi ₂ ^a	Ni:C
—	1380	50.4	1%	1:2
+	1475	55	5%	2:1
0	1437	52.7	3%	1:1

^a An amount of carbon equivalent to CaC₂ + SiC was added at each level.

randomized in blocks of four. All runs were made in indirectly heated reaction cells, in Ni tubes inside Vycor-glass furnace liners. Seed crystals (small macles) were placed in the powder mix about one-third the way along the major axis. An attempt was made to have the seeds not touch the walls of the cell.

No fluorescence or conductivity was found in any of the diamonds prepared in these experiments. In some cases, acid-resistant pieces of residual catalyst metal were found which had an unusual fibrous structure. These were identified by X-ray examination as δ -Ni₃Si. The reason for the separation of this

high silicon material is not readily apparent from the (room pressure) Ni-Si phase diagram, but it may well be formed during spectacular periodic composition fluctuations.

It was found that the only variable with a statistically significant effect at >95% probability is pressure. At the 90% probability level, temperature, pressure, temperature-pressure interaction, and temperature and pressure interactions separately with CaSi₂, concentration, and metal:carbon ratio are also significant. These results suggest that CaSi₂ does stabilize Ni₃C even at superpressure conditions and thereby effectively reduces diamond nucleation, since runs made under the same regime of pressure-temperature conditions in the absence of CaSi₂ produced consistently higher yields.

Some experiments were notable in that they produced an unusually high frequency of "macles" (rotation twins), especially at the upper limits of CaSi₂ concentration and at the higher pressures. Some of these twins were opaque and were found to contain large amounts of Ni. An attempt was therefore made to grow layers of boron-containing p-type diamond on seeds in the presence of CaSi₂, since it was hoped that the presence of Ni metal in the very finely dispersed form which had been observed might lead to a higher charge-carrier concentration and a higher conductivity in the stones. B-Doped material was therefore formed on natural macles at ~58 kbars, 1500°, using a graphite-CaSi₂ mixture and a Ni-0.16% B catalyst. However, no effect on the conductivity was seen when the products of these runs were compared with the controls.

In a set of experiments in which an 84% graphite-16% iron carbonyl dust mix was exposed to 1515°, 58 kbars for 10 min. in tantalum vessels, small amounts of dark green crystals were formed. When as little as 0.5% by weight of CaSi₂ was added considerable quantities of very much more lightly colored crystals were obtained. Similar great changes in appearance in diamond crystal yields were noted when up to 5% CaSi₂ was added to spectrographic graphite contained in a Co tube, and the whole exposed to 1425°, 58 kbars for 10 min. The runs without the dopant gave many irregular, hopped, and pagoda-like crystals; the dopant permitted the formation of larger and more regularly formed crystals, with exceptionally smooth faces.

High frequencies of occurrence of rotation twin crystals was also observed when Mg₂Si was used as a dopant in conjunction with a nickel catalyst. At 1400°, 50 kbars, 5% of Mg₂Si causes the formation of very lightly colored rotation-twinning diamond crystals from an 84% C-16% Ni mix.

(iii) **Experiments Involving Elemental Si.**—The effects of adding semiconductor-grade silicon to diamond-forming systems based on Fe, Ni, or Co catalysts were very similar to those seen when CaSi₂ or Mg₂Si were used, but they are particularly striking in Co systems. Normally, spectrographic grade graphite goes over to diamond so rapidly in the presence of Co (e.g., at 1350°, 57 kbars) that highly skeletal and other dendritic crystal forms are seen. The crystals are usually dark green and contain much metal. The addition of up to 5% of silicon causes the crystals to be lighter in color and well formed. They are also frequently of fine clarity.

(B) (i) **Quantitative Comparison of the Effects of B, Al, and Si on Nucleation.**—To examine the major effects in this system, the impurities were used at the 2% (atomic) level, in conjunction with pure nickel and pure graphite powders. Larger amounts of these elements were thought undesirable since they would permit the formation of well known binary compounds with nickel.

Al and Si were used as their carbides. Boron carbide is too stable for our present purpose, and this element was therefore employed as "adamantine boron," AlB₁₂, in which a tetragonal array of boron is stabilized by the presence of aluminum. All three materials were deliberately chosen at the "technically" pure level, again to assure the maximum chance of heterogeneous nucleation.

The SiC used was 4F carborundum. The Al₄C₃ was Union Carbide Electromet technical grade, which bore a general but remote resemblance to the attractive golden leaflets that we have prepared at high pressures and high temperatures. The AlB₁₂ was given to us by R. H. Wentorf. Its structural integrity was checked by the X-ray powder diffraction technique which yielded the listed tetragonal structure $a_0 = 10.28 \text{ \AA}$, $c_0 = 14.30 \text{ \AA}$.

A factorial experiment was run in which the effects of the impurities singly and combined were studied at a total impurity level of 2% (atomic), with respect to the sum of [B], [A], and [Si], and at the same temperature and pressure (~55 kbars, 1400°). The Ni-C base was a pure powder mix of atomic ratio

(4) M. Hansen, "The Constitution of Binary Alloys," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1958, p. 374.

1:1. All experiments were run in pure nickel tubes in Al_2O_3 -lined, indirectly heated, sample holders.

The diamond residues were separated mechanically from the alumina liner, and any excess of graphite and nickel was dissolved in the usual way. The diamond yields were weighed after being fractionated on a deck of standard sieves. Large yields were obtained, especially from those systems in which AlB_{12} was present. In addition, a few stones from runs in which Al_4C_3 and AlB_{12} were present together had a russet color, which had previously been observed⁵ in synthetic diamond only in Be-doped specimens. Further, a fairly large number of diamond crystals were seen to be overdeveloped columns with a length: breadth ratio of ~ 4 ; these occurred only in runs in which Al and Si impurities were simultaneously present.

The total yield response from each experiment was analyzed statistically. An external estimate of error variance was obtained by six Ni-C runs with no impurity present. The agreement between this estimate and the experimental between-block variance was satisfactory. Using these latter values the significance of the various treatment levels was examined. It was found that one variable, the main effect of the presence of AlB_{12} , was highly significant ($>95\%$). The treatment ($\text{Al}_4\text{C}_3 + \text{AlB}_{12}$) was significant at $90 + \%$ probability.

The shift in size distribution can also be examined for significant effect. The treatments (AlB_{12}), ($\text{Al}_4\text{C}_3 + \text{AlB}_{12}$), and ($\text{AlB}_{12} + \text{SiC}$) all cause a marked shift in size peak from $\sim 30\%$ on 60 and 80 mesh to $30 + \%$ on 140 mesh. The number density of nuclei is affected by a multiplier of ~ 10 , associated with the size change (note that size distribution in these residues of monocrystalline material are generally skewed, with the mode being larger than the mean, in terms of sieve size).

(ii) **Physical Examination of Crystals from the Above Runs.**—Comment has already been made on the columnar morphology of AlB_{12} -derived stones. A determination of the unit cell parameters of samples from runs involving various impurities gave results of 3.5667 ± 0.0006 (Al_4C_3) (a), 3.5681 ± 0.0005 (AlB_{12}) (b), 3.5669 ± 0.0005 (SiC) (c), 3.5667 ± 0.0004 ($\text{Al}_4\text{C}_3 + \text{SiC}$) (abc). The result for AlB_{12} is unusual and significant and was not obtained when boron was employed as a Ni-B alloy. These samples were also examined by electron spin resonance spectroscopy by C. M. Huggins and P. C. All gave patterns similar to that displayed by nickel-based diamond,⁶ that is, a broad resonance attributable to the presence of interstitial nickel surmounted by an intense triplet at $g = 2$, due to substitutional nitrogen. The only differences between samples were in the relative intensities of the triplet, which decreased in the order abc, a, b, c, and the height of the nickel band, which decreased in the order b, a, c, abc. At high dispersion the structure of the triplet became complicated by a general rise in the integrated absorption close to $g = 2$, which may be due to some kind of spin-spin interaction.

Discussion

(A) **Effects of Aluminum on Diamond Growth.**—Diamond nucleation is enhanced¹ in the presence of Al, compared with pure Ni catalyst, especially in the sense that good yields of small crystals are obtained when the pressure-temperature conditions are still quite near the threshold for Ni. The NiAl system is sensitive not only to the melting behavior of the composition used, but also apparently to the electron concentration of the composition. Diamond-nucleation densities for the reaction mix composition 2Ni:1Al:2C are typically in the range $5-10 \times 10^4/\text{cc.}$ compared with $1 \times 10^4/\text{cc.}$ for pure Ni, at the same conditions ($1525-1575^\circ$, 59 kbars). We have applied the terminology "co-catalyst" to the function of aluminum in promoting higher diamond nucleation density for a given transition metal catalyst.

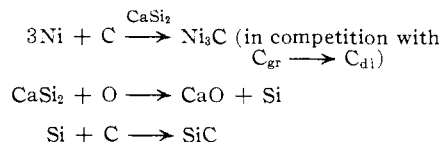
(B) **Effects of Boron.**—This element behaves in a way similar to Al in stimulating the nucleation of diamond, but its effects are much more marked. We, therefore, classify this substance also as a "co-catalyst" in respect to this reaction.

(5) R. H. Wentorf, Jr., private communication.

(6) C. M. Huggins and P. Cannon, *Nature*, **194**, 829 (1962).

(C) **Effects of CaSi_2 and the Nucleation of the 60° Rotation ("Macle") Twin.**—The nucleation mechanism of the twin habit is easily understood provided one considers a second phase to be responsible for the onset of twinning. We have found that natural macles do in fact contain such second-phase material, coherently attached to the diamond, which in general can be revealed only by differential cathodic etching.

If one assumes that the CaSi_2 in the present reactions serves to stabilize Ni_3C (which is normally stable only at high temperatures) until such time as there is sufficient oxygen to oxidize the calcium moiety, then one might expect the following type of set of reactions



It is apparent that something of this type is happening in that CaO and Ni were found *in* some of the diamonds. Naturally, the Si also will compete with the growing diamond for carbon. Now, the Si-C distance in hexagonal silicon carbide is almost exactly four-thirds the C-C distance in diamond, and the local symmetry of the silicon and carbon atoms is similar to that for carbon in diamond. Thus, it should be possible for fairly large patches of SiC to nucleate on the nascent (111) face of diamond. The structure of (6H) hexagonal SiC is most easily expressed as a composite of face-centered cubic material, rotated by 60° every third atom layer. Thus, once some SiC has nucleated on a 111 diamond face, there is a good chance (two out of three) that as the system goes lean in Si and diamond renucleates, that the new diamond will be off orientation by $\pm 60^\circ$, and the nucleus of the macle will thus exist (Fig. 1).

It is theoretically possible for this nucleus to be formed if the second phase is simply hexagonal carbon which can easily be seen to have equivalent 60° structural rotations, especially in the case of *abcabc* graphite which is believed to be a favored form at high pressures. This would explain the (infrequent) occurrence of macles in experiments in which Si-releasing materials were not present; the only necessary condition for this phenomenon is that one should operate very near the graphite-diamond phase boundary, so that neither phase is exceptionally stable with respect to the other. This would seem to be relevant to the problem of forming regular new growth on a seed since the necessary conditions for the suppression of new nuclei are very near those described for polytypism.

The effect of a decomposable silicon-containing compound on the reaction thus leads to decreased yields of more slowly grown diamond crystals when nickel is used as a catalyst base. Very similar results are found when cobalt and cobalt-based alloys are used and the diamond formed is of unusual surface perfection. In addition, the formulation of rotation twins is understandable in terms of simultaneous formation of hexagonal silicon carbide.

(D) **Quantitative Study of Impurities Introduced as Stable Compounds.**—The striking feature of the experiments in which SiC, AlB_{12} , and Al_4C_3 were used as impurities is the over-all similarity of the results to those obtained using pure Ni alone. The only real

differences seen were with the impurity AlB_{12} ; we are led to conclude that for substituent impurities to appear in the diamond product they must be present in the catalyst at the time of diamond nucleation. In the present case, the impurity AlB_{12} is almost certainly most easily incorporated into the nickel in the reaction time (20 min.), and we also note that the interaction treatments ($\text{Al}_4\text{C}_3 + \text{AlB}_{12}$), ($\text{AlB}_{12} + \text{SiC}$), and ($\text{Al}_4\text{C}_3 + \text{AlB}_{12} + \text{SiC}$) (*abc*) appear in large measure to be controlled by the treatment of AlB_{12} . In fact, only the interaction *abc*, in which the concentration of AlB_{12} is one-third that in *b* (AlB_{12} alone), appears to differ in its nucleation characteristics from the other treatments containing *b*.

(E) Effects of Substances Introduced as Poisons.—

Oxygen does not function as a poison in the presence of free silicon (which can reduce CO to C up to 1800°K.) and, under such circumstances, diamond can be found intergranularly in the by-product silica. Since the latter was undoubtedly formed while the diamond was also formed, it is possible that the diamond was preferentially located in the liquid oxide phase. It was further found that if free transition metal had been initially charged to the system, diamond was frequently formed, even in the presence of quite large amounts of oxygen combined as stable oxides or as carbonates. It is possible then that oxygen acts as a poison only through CO formation, leading to electron donation to the transition metal.

(F) General Discussion.—The observed nucleation densities (as high as $10^6/\text{cc.}$) and the absence of nucleation upon such *added* substances as SiC indicate that the formation of diamond does not in general depend on the presence of foreign heterogeneous nuclei. Further consideration of the results indicates that although the process may well depend on homogeneous nucleation, the latter is sensitive to the precise chemical nature of the transition metal catalyst, so that impurities present in the latter can be found in the diamond. It is also significant that thermodynamic equilibrium is not necessarily attained during the reaction time (*e.g.*, 20 min.), so that the yield of the reaction is found to vary strongly with the chemical conditions. It is important to note that diamond growth may cease within this period of time, suggesting that either some (unspecified) catalyst function of the metal has been destroyed, or that the carbon transport pathway to diamond has been closed, or that both effects are operative. Both will depend on the presence of impurities, but it seems unlikely that the second would show the observed variation depending on acceptor-donor properties with respect to carbon.

It will have been noted that little evidence or discussion of the effects of nitrogen has been given. This is primarily because of the difficulty of controlling the input of this substance since it is always present in the graphite conventionally used in these experiments. However, in view of the fact that nitrogen does appear in laboratory-prepared diamond in quite large amounts, an effort will be made to trace the fate of this element using N^{15} as a marker.

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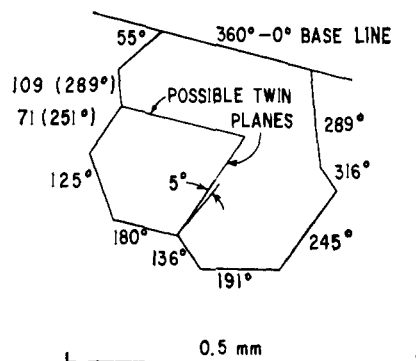


Figure 1.

Appendix

Possible Origin of Color of Doped Diamond.—There is a wide variation in the color of diamond prepared using different catalysts, and this variation is particularly strong for diamond containing light atom impurities. In general, the presence of Al, B, and Be yields colorless, blue, and red-brown diamonds, respectively, while pure Ni gives a yellow-green product, Co green crystals, and Fe a relatively colorless but brownish yield. There is, however, a difference between the effects of a specific catalyst metal and those of impurities; the former are dependent on pressure-temperature conditions but do not vary strongly with initial catalyst concentration, while the intensities of the latter are primarily dependent on initial impurity concentration, above a certain minimum value. It seems unlikely from these last facts that Ni, Co, and Fe contribute directly (by incorporation in the growing diamond) to the optical absorption seen in the undoped cases, but rather that the variation in greenish hue is due to nitrogen, which is known to be present in natural⁷ and laboratory-prepared diamond,⁶ or to defects peculiar to the diamond lattice.⁸

We now offer a correlation of the colors seen in Al-, B-, and Be-doped diamond with an elementary single-bond energy model. Justification for this approach may be gleaned from the large nuclear charge screening inherent in the middle elements of a period, and the fact that this discussion concerns elements in the first two periods, where spin-orbit coupling is small and simple quantum rules are strongly obeyed. It is odd but true that if laboratory-prepared diamond has an absorption edge at 5.2 e.v. the role of the above acceptor impurities in coloring the crystal can be understood.

Consider the general case of a lattice of quadrivalent atoms X, ionization potential x , and a trivalent accep-

(7) W. Kaiser and W. L. Bond, *Phys. Rev.*, **115**, 857 (1959).

(8) F. C. Champion, *Phil. Mag. Suppl.*, **5**, 383 (1956).

tor impurity Y, ionization potential y . Let both a pure X lattice and an X lattice containing y be ionized, the charge center being at a Y atom in the latter case. The difference in energies of these two states is simply $(x - y)$, and this represents the depth of the impurity level below the conduction band, since the first case corresponds to photoexcitation of the host. The transition from the valence band to the impurity level is permitted if $x - y$ is positive, and we can thus derive the following results for heavily doped Ni-based diamond (Table II). These calculations are confirmed by the results of several hundred experiments in these systems, though the nearest we have come to a true red diamond is a russet-brown hue by Be-doping or by very heavy doping with B, Al, and Si combined. The results here are doubtless complicated by the possibility of multiple ionization processes. The anticipated effect of Si alone in

TABLE II
SINGLE BOND-ENERGY CALCULATION FOR IMPURITIES
IN DIAMOND

	x	y	$x - y$	5.2 - ($x - y$)	Absorp- tion	Crys- tal color	Color obsd.
X = C, Y = B	11.26	8.30	2.96	2.2	Red	Blue	Blue
Al	11.26	5.98	5.29		Infrared	None	None
Be	11.26	9.32	1.94	3.3	Blue	Red	Russet

small quantities would be to give absorption in the near-red; this may be the cause of some of the more desirable colors of natural diamond. The same is true of calcium, which is also found as a frequent trace impurity in natural stones. Qualitative agreement with these latter predictions has been observed, as described. A more sophisticated treatment should take some account of the possibility of compensated nitrogen centers⁷ affecting the absorption.

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The Determination of the Geometry of High-Temperature Species by Electric Deflection and Mass Spectrometric Detection^{1a}

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The electric deflection of mass spectrometrically detected molecular beams has been used to study the molecular geometry of high temperature species by determining whether they possess permanent dipole moments or not. By this means it has been shown that (1) the lithium halide dimers are planar; (2) lithium oxide, Li_2O , is linear; (3) the beryllium and magnesium dihalides are linear; the barium dihalides are bent; (4) the group IIB dihalides are linear; (5) the dihalides of the transition metals from manganese through copper are linear; (6) the lead dihalides are bent. Both PbI and PbI_2 were found in lead iodide vapor. Many of the structural results are in disagreement with the prediction of simple theories of molecular geometry.

The importance of the electric dipole moment in molecular structure determination is well known.^{2,3} Today there exist several experimental techniques for determining molecular structures which were unavailable as recently as 20 years ago and which are capable of very high precision and reliability. Crude structural determinations by means of electric polarity might therefore be regarded as retrogressive. In one area, however, the chemistry of high temperature systems involving polyatomic species, sophisticated spectroscopic methods have been difficult to apply, and a return to earlier techniques therefore appears to be useful.

The probable complexity of the vaporization of simple inorganic compounds was first stressed by Brewer. He pointed out that the complexity of the saturated vapors would most likely increase with increasing temperature, since the entropy ($-T\Delta S$) term of the free energy would eventually overwhelm any unfavorable enthalpy (ΔH) value. Since Brewer and Lofgren's pioneering work on the vaporization of cuprous chloride⁴ in which the existence of Cu_3Cl_3

was demonstrated, a large number of polyatomic molecules have been shown to exist in saturated vapors at all temperatures investigated, *i.e.*, to approximately 3000°K . These species have been identified principally by mass spectrometric analysis of the vapors.⁵ The variety of species which have been found in this way is well illustrated by a list of gaseous polyatomic alkali compounds. The 1959 review cited⁵ lists halides,⁶ oxides,⁷ and hydroxides.⁸ Since that time, gaseous alkali cyanides,⁹ metaborates,¹⁰ nitrates,¹¹ and molybdates,¹² as well as mixed alkali-beryllium,¹³ alkali-aluminum,¹⁴ and alkali-transition metal halides,^{13,15} have been shown to exist.¹⁶

(4) L. Brewer and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 3038 (1950).

(5) M. G. Inghram and J. Drowart, "Proceedings of the International Symposium on High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 219.

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(8) R. F. Porter and R. C. Schoonmaker, *J. Chem. Phys.*, **28**, 168 (1958).

(9) R. F. Porter, *ibid.*, **35**, 318 (1961).

(10) A. Büchler and J. B. Berkowitz-Mattuck, *ibid.*, **39**, 286 (1963).

(11) A. Büchler and J. L. Stauffer, unpublished work.

(12) A. Büchler, J. L. Stauffer, W. Klemperer, and L. Wharton, *J. Chem. Phys.*, **39**, 2299 (1963).

(13) J. Berkowitz and W. A. Chupka, *Ann. N. Y. Acad. Sci.*, **79**, 1073 (1960).

(14) R. F. Porter and E. E. Zeller, *J. Chem. Phys.*, **33**, 858 (1960).

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(16) The existence of many of these species was in fact implied in the molecular beam experiments of S. Millman, P. Kusch, and I. I. Rabi, *Phys. Rev.*, **55**, 666, 1176 (1939); **56**, 165, 303, 527 (1939); **60**, 91 (1941).

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