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Identification of cobalt on a lattice site in diamond

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We report the finding of an electron-paramagnetic-resonance (EPR) center, labeled O4, which contains cobalt on a site in the diamond lattice. O4 is observed at low temperatures (<30 K) in high temperature and pressure synthetic diamonds grown with a cobalt containing metal-solvent catalyst after a high-temperature anneal at 1800 °C. The center has $S=1/2$, monoclinic I symmetry and a hyperfine splitting from a nucleus with $I=7/2$. Analysis of the measured hyperfine interaction in terms of $3d^5$ gives the unpaired electronic wave function on the cobalt atom, and correctly predicts the measured **g** matrix. The wide linewidth of the EPR absorption suggests a small hyperfine interaction arising from a nearby nitrogen atom. Based on this evidence, a model for O4 is presented in terms of a CoN complex.

Although many elements of the Periodic Table have been found in diamond, only boron, nitrogen,[1] and nickel[2,3] have been shown to occupy sites in the diamond lattice. This paper describes a defect detected by electron-paramagnetic-resonance (EPR), which comprises a cobalt atom at a site in the lattice of a high temperature and pressure synthetic diamond.

The diamond was grown at the De Beers Diamond Research Laboratory in Johannesburg using a cobalt containing metal-solvent catalyst. As grown, the sample exhibited a photoluminescence (PL) system with a zero phonon line (ZPL) at 1.989 eV. The nitrogen concentration of the sample measured by Fourier Transform Infrared Spectroscopy (FTIR) showed that the sample had 320(20) parts per million (ppm) of single substitutional nitrogen (P1) and no other aggregation.[1] After annealing at 1800° C for 20 h the 1.989 eV system vanished with the appearance of ZPL's at energies of 2.135, 2.207, 2.227, and 2.590 eV observable in both PL and cathodoluminescence.[4] In addition, FTIR and EPR measurements showed that there had been a 91% conversion of single substitutional nitrogen centers into *A*-centers (nearest-neighbor pairs of substitutional nitrogen atoms), leaving 25(3) ppm of P1 centers and 3.4(5) ppm of the ionized P1 center N^+.[5] In addition a new EPR defect, which in the tradition of naming EPR centers in diamond we label O4, is observed at low temperatures (<30 K) with concentration ~ 0.2 ppm.

EPR measurements at 9.5 GHz and 5 K show a spectrum with an extensive structure and a complicated angular variation: Fig. 1 shows this angular variation in a $\{110\}$ plane. When the external Zeeman field **B** is along a symmetry direction: $\langle 100\rangle$, $\langle 111\rangle$, or $\langle 110\rangle$, and also along certain other directions, the spectrum clearly comprises groups of eight equally intense lines separated by about 7.6 mT (Fig. 2). This corresponds to hyperfine structure from a nucleus with nuclear spin $I=7/2$. As these are the only observed lines, this must correspond to an element without isotopes with $I=0$, and where any other isotopes have very low ($<5\%$) abundance or also have $I=7/2$ and an almost equal nuclear moment. Several isotopes satisfy these criteria: ^{45}Sc, ^{51}V (99.75), ^{59}Co, ^{133}Cs, several lanthanides and ^{181}Ta (where the natural isotopic abundance is given in brackets if it is less than 100%). The short length of the C-C bond (0.154 nm) in diamond makes it unlikely that all but the first three are incorporated into the diamond lattice. Since the sample was grown with a solvent catalyst containing a large proportion of cobalt, and O4 has not been observed in samples grown in other conditions, the identification with cobalt is certain.

The whole complex spectrum shown in Figs. 1 and 2 can be accounted for by 12 equivalent sites of one single type of center (O4) with monoclinic I symmetry, generated by the symmetry operations of the diamond lattice. The spectrum is described by the following spin Hamiltonian, where all terms have their usual meaning,

$$\mathcal{H}=\mu_B\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}-\mu_N g_N\mathbf{I}\cdot\mathbf{B}+\mathbf{I}\cdot\mathbf{P}\cdot\mathbf{I} \qquad (1)$$

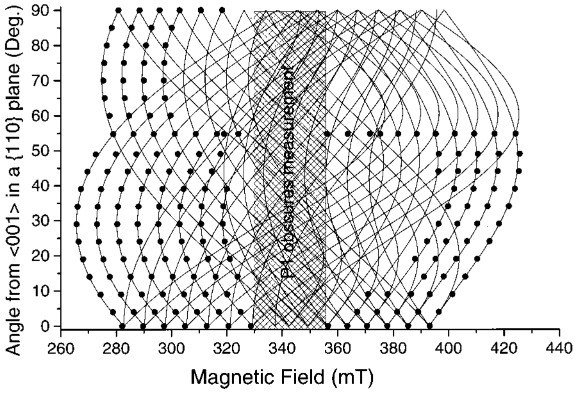

FIG. 1. Angular dependence of the EPR transitions from O4 centers for rotation about a $\langle 110\rangle$ axis, with θ measured from a $\langle 001\rangle$ direction. The circles are experimental data, measured at frequencies of around 9.59 GHz. The solid lines are calculated at 9.59 GHz using the **g** and **A** matrices determined from fitting the experimental points to the spin Hamiltonian described by Eq. (1). See text for further details.

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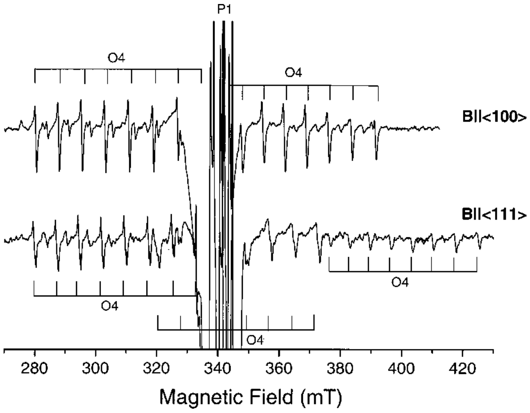

FIG. 2. First harmonic EPR spectra taken at 5 K, with a microwave frequency of approximately 9.59 GHz and an incident microwave power on the TE_{011} resonant cavity of 6 μW. See text for further details.

with $S=1/2$ and $I=7/2$. The spin-Hamiltonian parameters of the first two terms are listed in Table I. The parameters of the final term, describing the quadrupole interaction, have not been measured; but the need of this term is indicated by the presence of *forbidden lines* corresponding to transitions with $\Delta M_S=1$, $\Delta M_I=1$ or 2, which lie between the eight nearly equally spaced *allowed transitions* with $\Delta M_S=1$, $\Delta M_I=0$ (Fig. 2). The observed angular variation corresponds to symmetry of C_{2h} or C_{1h}. That the symmetry of the defect is not lower was established by observing that the lines corresponding to a single site in Fig. 1 do not split on rotating **B** out of the $\{110\}$ plane. The line width of O4 was ~ 0.8 mT, rather wider than the width of the P1 spectral lines in the same sample (~ 0.1 mT).

The identification of the defect as an unpaired electron interacting with a ^{59}Co nucleus described by a single-spin Hamiltonian, shows that the cobalt occupies a specific site in the diamond lattice. The large hyperfine interaction with ^{59}Co, similar in magnitude to that in cobalt salts,[6] indicates that the paramagnetism arises from $3d$ electrons located on the cobalt atom. The properties of the site so far measured allow some deductions about its nature, the principal evidence being the symmetry of the site and the difference between the principal g values and the free spin value g_e.

The low symmetry of the site is unlikely to arise from a purely substitutional or interstitial site. Without distortion, such sites usually have much higher symmetry; and, although for an appropriate $3d$ configuration, one might have a Jahn-Teller distortion, it is not necessary for the symmetry to become as low as C_{2h} to raise the orbital degeneracy that causes it. With the exception of the P1 center[1] and the neutral divacancy,[7] the R4/W6 EPR center, which was found to have C_{2h} symmetry, rather than the expected D_{3d} symmetry, all known defects in diamond have the symmetry of their site.

TABLE I. The **g** and **A** matrices of the O4 center determined at *X* band (9.59 GHz). The angles $[\theta,\phi]$ refer to spherical coordinates expressed in the crystal cubic axis system. In the final fit g_x and A_x were constrained along the [90°, 315°] direction. Removing this constraint did not improve the quality of the fit.

g matrix		**A** matrix (MHz)	
$\lvert g_x\rvert=1.8438(5)$	[90°, 315°]	$\lvert A_x\rvert=180(2)$	[90°, 315°]
$\lvert g_y\rvert=1.7045(5)$	[61(2)°, 45°]	$\lvert A_y\rvert=163(2)$	[65(2)°, 45°]
$\lvert g_z\rvert=2.3463(5)$	[151(2)°, 45°]	$\lvert A_z\rvert=248(2)$	[154(2)°, 45°]

We therefore expect that the low symmetry of the site is the result of complexing with other atoms; an association of a cobalt atom with a vacancy or impurity. A likely impurity is nitrogen, since the sample, as grown, contained more than 300 ppm of nitrogen and under the conditions of the anneal nitrogen is known to be mobile.[8] In nickel-containing diamonds, a variety of nickel-nitrogen aggregates are found after a similar anneal.[9] Although for O4, no ^{14}N hyperfine structure (hfs) is resolved, the unusually wide lines indicates unresolved ^{14}N hfs. Microwave saturation measurements at 4.2 K and comparison with the intrinsic linewidth of P1 (~ 0.1 mT), showed that the large linewidth of O4 is not caused by spin-lattice relaxation or spin-spin broadening.

The site symmetry requires that the cobalt atom and any perturbing vacancy or nitrogen atom should lie in the $\{110\}$ plane of reflection symmetry. The electronic configuration of the cobalt will depend upon the nature of the site. Neutral cobalt has nine electrons outside its closed $3s$ and $3p$ subshells. If the cobalt forms n covalent bonds with its neighbors, n of its electrons will be used up in the bonds.[10] So for a charge of qe, the configuration of the unpaired electrons on the cobalt atom will be $3d^{9-n-q}$. For $S=1/2$, the number of unpaired electrons must be odd. The presence in the sample of a large concentration of donor nitrogen and measured concentration of ionized nitrogen N^+ greater than the concentration of O4, makes it very likely that q is zero or negative. For a substitutional site $n=4$, so the configuration would probably be $3d^5$. The crystal field splits $3d$ orbitals into the subsets e and t_2.[2,3,10] In a strongly bonded tetrahedral site, $3d^5$ would be e^4t_2, which would be like t_2 in an octahedral site where g values are all much less than g_e, contrary to the observations. For an interstitial site $n=0$, so the configuration would probably be $3d^9$, which at a tetrahedral site would be $e^3t_2^6$, since the octahedral crystal field from the next-nearest neighbors is dominant over the tetrahedral field of the nearest neighbors.[10] If this were distorted by an atom at a third neighbor site, a site diametrically across the *chair*, it would produce the observed symmetry.

Another possibility is a defect structure like those reported in nickel containing diamonds, NE1-8,[9] where a paramagnetic atom takes up a semivacancy position, so that it can form six almost octahedrally coordinated bonds with the carbon neighbors $[CoC_6]$, when $n=6$. For strongly bonded neutral cobalt that would give t_2^3, $S=3/2$, at a site of D_{3d} symmetry, and g values very close to g_e, contrary to the observations.

The observed site has g values very similar to those observed in strong-bonded octahedral complexes of t_2^5, $S=1/2$, with a mean g value less than g_e.[6] A way in which such a configuration with the observed symmetry could be formed is by incorporating a nitrogen atom into the ligand shell, and also accepting an electron from another nitrogen donor, so that the site could be regarded as $[CoC_5N]^-$ (shown in Fig. 3). This is analogous to the NE1-8 defects,[9] which have the form $[NiC_yN_{6-y}]^q$. The presence of the N

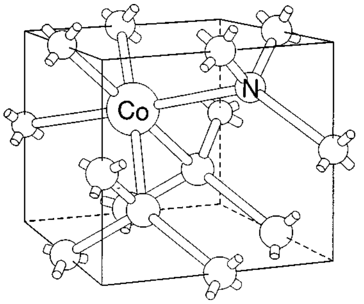

FIG. 3. The model proposed for O4. The Co is sixfold coordinated at the bond-centered site between two vacancies, with a nearby N atom in the {110} plane of reflection symmetry of the defect. See text for further details.

ligand would lower the symmetry from D_{3d} to C_{1h}, and as the hole in the t_2 shell does not σ-bond with the octahedrally placed ligands, one expects any ligand hyperfine interaction to be small. If we assume that the wide linewidth (0.8 mT) of O4 is a consequence of nitrogen hyperfine broadening from a single nitrogen, then using the standard linear combination of atomic orbitals treatment, this suggests $\sim 8\%$ of the unpaired electronic wave function on the nitrogen.

Bleaney and O'Brien derive expressions for the principal g values for the configuration t_2^5 in a strong crystal field of distorted octahedral symmetry.[11] Their equations:

$$g_z = 2\cos^2\theta[\sin^2\alpha - (1+k)\cos^2\alpha] + 2\sin^2\theta[k-1], \quad (2)$$

$$\frac{1}{2}(g_x+g_y) = -2\cos^2\theta[\sin^2\alpha - \sqrt{2}k\cos\alpha\sin\alpha], \quad (3)$$

$$\frac{1}{2}(g_x-g_y) = -2\sin 2\theta[\cos^2\alpha + (k/\sqrt{2})\sin\alpha], \quad (4)$$

involve three parameters, θ and α, which describe the admixture of t_2 orbitals in the ground state and depend upon the crystal field, and an orbital reduction factor k. The best fit to our measured values in Table I, calculated for $k=1$ corresponds to

$$g_x = -1.852, \quad g_y = -1.712, \quad \text{and} \quad g_z = -2.402, \quad (5)$$

with $\alpha = 31°$ and $\theta = -0.8°$. The small differences between these values and the experimental values suggest that k ~ 0.96. Bleaney and O'Brien[11] state that there is no clear correlation between the principal directions of the **g** matrix and the crystal field, so it is not clear whether any conclusion can be drawn from the fact that the measured principal direction of g_x is nearly normal to the (332) plane defined by four of the carbon ligands. The parameters represent quite a small distortion from cubic symmetry,

Bleaney and O'Brien also give expressions [Eq. (9) in their paper[11]] for the principal values of the hyperfine interaction with the ^{59}Co nucleus in terms of the same parameters θ and α, and a core polarization factor κ, which Abragam and Pryce[12] show to have a value of 0.33 for Co^{2+} salts, and the parameter $P = 2g_N\mu_N\langle r^{-3}\rangle$. Our hyperfine interactions in Table I correspond to values of P ranging from 218 MHz to 173 MHz, which considering the low symmetry of O4 is respectable internal consistency. In principal, one should be able to deduce the spin density on the cobalt nucleus from this value, but it requires extrapolation of the value of P for Co^- in a covalent surrounding from the known value (675 MHz) for Co^{2+} in ionic crystals.[12] Abragam and Bleaney[6] tabulates values of $\langle r^{-3}\rangle$ for ions Co^{4+} to Co^+, which show a fairly consistent fall of 11% per unit of charge reduction. Using this extrapolation gives 480 MHz for Co^-, which suggests that our measured hyperfine parameters correspond to a charge density of about 40% on the cobalt atom.

To conclude, $[CoC_5N]^-$ appears to be the most likely model for O4, and it is a type of defect that has precedent in the structures formed by the next atom in the Periodic Table, nickel. Further experiment, such as ^{14}N ENDOR, or EPR of ^{13}C hyperfine structure in an isotopically enriched sample, will be needed to establish the model beyond doubt. This paper has shown that the cobalt atom can be incorporated into a site in the diamond lattice.

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