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Lattice dynamics of isolated nitrogen in synthetic diamond

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The effects of isolated nitrogen impurities on the bulk phonon spectrum of synthetic diamond are investigated using a model in which the nitrogen atom is part of an eight-atom impurity cluster in the lattice. Good agreement with experimental results is obtained. The physical basis for the unusual isotope-dependent behavior of two prominent impurity modes is determined.

INTRODUCTION

It has long been known that nitrogen impurities in natural diamond cause single-phonon modes.[1,2] From efforts that have been made to decompose the spectrum into components due to different aggregate forms,[3] it appears that the primary form is created by pairs of substitutional nitrogen atoms forming a defect with trigonal symmetry that makes a contribution to the absorption spectrum denoted as a type-A spectrum. Significant contributions to the spectrum also arise from more complex aggregates of nitrogen called type-B and -D clusters.[4–6] The type-B defect is an agglomerate containing four nitrogen atoms and the type-D defect is thought to be an aggregate of nitrogen atoms containing an unknown second impurity.[7] Diamonds containing A and B defects are generally referred to as type-Ia diamonds. While contributions from isolated nitrogen atoms can be expected, they are masked by those of the more complex defects. The reverse is true in synthetic diamond where the density of nitrogen is much smaller than that for natural diamond. In this case one finds primarily isolated substitutional nitrogen impurities.[8] The absorption spectrum caused by a low concentration of nitrogen has a characteristic shape and such diamonds are called type-Ib diamonds. Study of the effects of isolated nitrogen defects on the phonon spectrum of type-Ib synthetic diamond will allow us to obtain detailed information regarding lattice distortions and interatomic-force-constant changes due to a single impurity.

Experiments on the infrared absorption properties of type-Ib synthetic diamond crystals in the single-phonon region yield an absorption curve with several interesting features. These include a broad band peaking at 1130 cm^{-1}, a flattish hump between 1200 and 1332 cm^{-1}, a broad peak at about 1090 cm^{-1}, and a very sharp peak close to 1344 cm^{-1} (see Fig. 1). These features are all ascribed to the presence of isolated substitutional nitrogen impurities. Of particular interest are the nitrogen-induced peaks at 1130 and 1344 cm^{-1}. This is because while both modes are due to the presence of nitrogen, only the 1130-cm^{-1} mode is directly isotope dependent, shifting to a lower frequency when ^{15}N is substituted for ^{14}N. The 1344-cm^{-1} peak does not shift as one might expect thus indicating only an indirect dependence on the presence of nitrogen.[9] The reasons behind this behavior are not well understood and the purpose of this work is to explain that behavior.

Our approach is based on several considerations. Both modes are due to the presence of isolated nitrogen atoms. The isotope-dependent mode is in the main band of the diamond spectrum as one would expect because the impurity mass is greater than the host lattice mass, resonance modes are dependent on the ratio of the central force constant to the mass, and there is no reason to expect the central force constant to deviate greatly from the host lattice value. On the other hand, the isotope-independent higher-frequency modes lies outside the main band and would require a value of the central force constant greater than the host lattice value. The origin of these two modes cannot be attributed simply to the mass difference and change in force constant between the nitrogen and its carbon nearest neighbors. Our preliminary results also show that inclusion of changes in possible

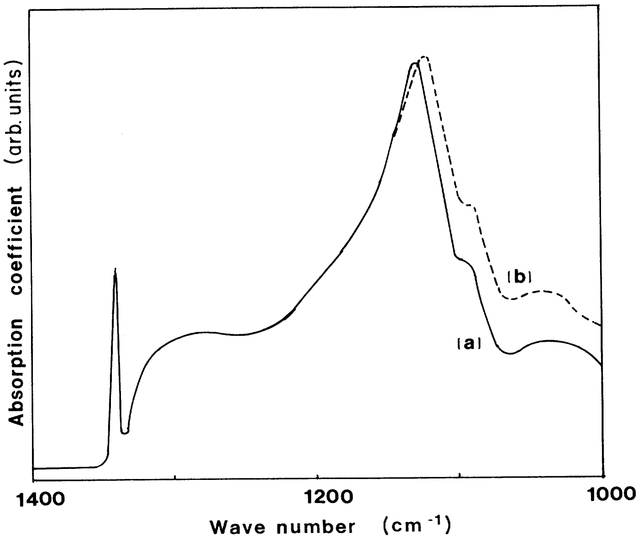

FIG. 1. High-resolution absorption spectra in the one-phonon region for (a) a ^{14}N-containing sample, and (b) a diamond containing roughly equal concentrations of ^{14}N and ^{15}N (reproduced from Ref. 1).

second-neighbor interactions cannot decouple the isotope dependence of the two impurity modes.[10,11] Hence the isotope-dependent behavior of the two modes is not simply explained.

A major clue to the solution of the problem comes from experimental results[12–14] that show that the nitrogen atom is displaced off center from the normal lattice site toward three of its four nearest carbon neighbors. This displacement may be explained in terms of a weakened bond between the nitrogen and the fourth carbon nearest neighbor. This weakening of a C—N bond may be attributed to the itinerant electron provided by the nitrogen being captured in the antibonding state of a CN pair, inducing a weakening in the bonding of that particular CN pair. As a result, that carbon nearest neighbor will also be displaced toward its three carbon nearest neighbors. Our approach, thus, was to consider that the substitutional nitrogen creates a weakly bound CN pair which then forms part of an eight-atom impurity cluster. In this cluster the nitrogen has three equivalent carbon nearest neighbors and the weakly bound carbon has three of its own equivalent carbon nearest neighbors. Thus, there are eight different sites to be considered. Within this eight-atom cluster the interactions between the nitrogen and its neighbors will be different than the interactions between the CN carbon and its carbon neighbors. Also, the carbon nitrogen interactions of the CN pair will be different from the other interactions. It is this isolated CN pair and its six nearest neighbors which form the impurity cluster whose effect on the diamond spectrum we will attempt to determine.

The connection with experiment will be made through the local density of states (LDOS) which will be compared with the experimental absorption curves.[1] Because there are eight sites involved, the total local density of states, (TLDOS) of the defect configuration will be a weighted linear combination of eight site-dependent densities of state.

We have seen how certain site-dependent contributions have an isotope dependence in agreement with experiment in that the lower-frequency mode was isotope dependent but the higher mode was not.[11] We also obtained good agreement for the TLDOS for ^{14}N in terms of the overall shape of the spectrum and location of the two modes of interest. However, when we later constructed the TLDOS for ^{15}N, we found that the isotope shift for the low-frequency mode had disappeared. This is because the isotope-dependent peak can be masked by an isotope-independent mode arising from the carbon site contributions to the LDOS and we used that knowledge to refine our considerations. In the following sections we present details of this consideration.

THEORY

Since we are dealing with isolated impurities we expect the local environment to play a significant role in determining the vibrational properties of the impurity modes and therefore will need to be accurately represented in any analysis. In that regard we have developed an effective real-space approach to the calculation of the phonon density of states in which no approximation is made for the underlying lattice structure.[15] We use the recursion method to write the local Green's function G_{ll} as a continued fraction and obtain the local density of states for any site as the limit of the imaginary part of G_{ll},

$$\rho_l = -\frac{1}{\pi} \lim_{\epsilon \to 0} \operatorname{Im} G_{ll}(\omega^2 + i\epsilon) \ . \tag{1}$$

Since we are interested in the effect of isolated substitutional nitrogen atoms we would ordinarily concentrate on the nitrogen site only, but the considerations presented in the Introduction require a more general outlook. Ordinarily, one would think that a substitutional impurity in a diamond lattice would be part of a five-atom cluster with T_d symmetry. However, experiment has shown that the nitrogen impurity is displaced from the normal lattice site forming a cluster having C_{3v} symmetry with its three nearest neighbors leaving the other carbon neighbor to form a similar cluster with its three nearest carbon neighbors. Thus, instead of a single isolated impurity we are led to consider an impurity cluster composed of a weakly bound C—N pair together with its six nearest neighbors, the nitrogen having three equivalent carbon neighbors and the CN carbon having three different equivalent carbon neighbors. It is the density of states of this eight-atom cluster that we need to obtain.

In calculating the total LDOS for this cluster we used the nearest-neighbor approximation, which is characterized by two parameters: α, which gives the central force interactions and β, which gives the noncentral force interactions. While the nearest-neighbor approximation does not provide the best possible results for the phonon spectrum of the bulk diamond lattice, inclusion of second-neighbor interactions here would simply complicate the issue. We are interested in the basic physical processes and the nearest-neighbor approximation should suffice in that our conclusions must be independent of the precise values of the interactions. Second-neighbor interactions should only modify our conclusions in degree and not in significance.

The cluster density of states, TLDOS, is composed of eight site-dependent densities of states which in turn depend on the displacement vector at that site so that each of the site-dependent densities of states has three components, one for each of the three directions x, y, or z. Using a numbering scheme where site 1 is occupied by nitrogen, site 2, called C(2), is occupied by its weakly bound carbon companion, sites C(3), C(4), and C(5) are occupied by the three equivalent nearest neighbors of the nitrogen atom, and C(6), C(7), and C(8) are occupied by the three equivalent nearest neighbors of the carbon at C(2) (see Fig. 2), the cluster density of states may be written as

$$\rho(\omega^2) = \frac{1}{24} \left[\sum_{\mu} \rho_\mu(N) + \sum_{\mu} \rho_\mu(\mathrm{C}(2)) + \sum_{\mu,\nu} \rho_{\mu,\nu}(\mathrm{C}(\nu)) \right] , \tag{2}$$

where $\mu = x, y$, or z and $\nu = 3, 4, \ldots, 8$.

By symmetry arguments, supported by direct calculation, we were able to reduce the total number of site

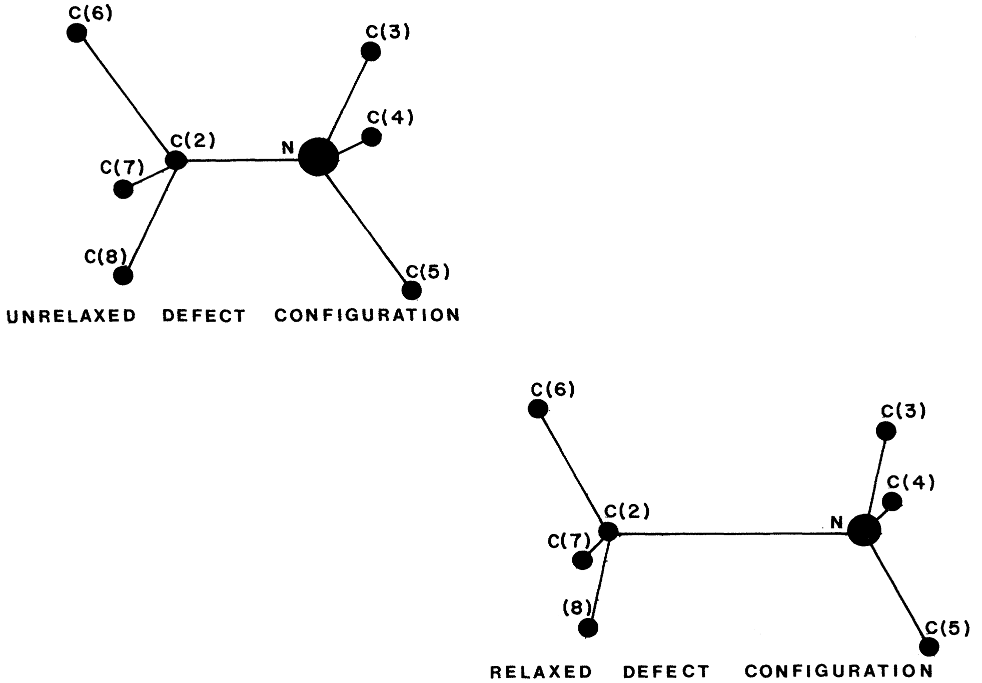

FIG. 2. Stick figure drawing of the eight-atom cluster showing the labeling of the sites.

LDOS's to be calculated. We found that the three components of the site LDOS centered at the nitrogen site $\rho_\mu(N)$ were equal as were the three components of its carbon companion at C(2). However, for the six carbon neighbors of the CN pair only certain equalities were found to hold depending on the site. For each of those sites two of the three components were found to be equal to each other, but which two were equal depended upon the site. In this way the cluster LDOS became

$$\rho(\omega^2)=\tfrac{1}{8}[\rho_x(N)+\rho_x(\mathrm{C}(2))+\rho_z(\mathrm{C}(3))+\rho_z(\mathrm{C}(6))] \\ +\tfrac{1}{4}[\rho_x(\mathrm{C}(3))+\rho_x(C(6))] \; . \qquad (3)$$

With the concept of the impurity cluster in the nearest-neighbor approximation we have three different pairs of interaction parameters (α,β). There is the interaction between nitrogen and its three equivalent neighbors, between the carbon at C(2) and its three equivalent nearest neighbors, and between the nitrogen and the carbon of the CN pair at site C(2).

For each set of interactions the values of the site-dependent LDOS's were obtained from the continued fraction obtained through the recursion method. The continued fraction is completely determined by a set of recursion coefficients (a_n, b_n). We calculated 35 pairs of recursion coefficients exactly (corresponding to a group of 34 273 sites) and then expanded the set to 200 pairs as described by Zhou, Wu, and Dy.[16] The imaginary part of Eq. (1), ϵ, was determined as described by Sinai and Wu.[17] To determine an appropriate value for ϵ, the spectrum was calculated for decreasing values of ϵ until the overall features of the spectrum stabilized.

RESULTS

The general effects of varying the force constants, α and β, for an isolated impurity on the phonon spectrum were examined in an earlier work.[17] There it was found that the location and general shape of the impurity spectrum were controlled primarily by the central force constant α, whereas the noncentral force constant β controlled the spacings and fine structure of those modes. Thus, our intent here was to adjust the different α values first with reasonable β values to obtain the general shape of the total spectrum with the two modes close to the desired locations and then make minor adjustments to the spectrum through variation of the different β values.

This situation is different from the previous case in that there are now three pairs of interaction parameters instead of one. It first appears that with three pairs of parameters there is too much latitude. Yet, in addition to the physical limitations, there are interrelations among the pairs such that a change in one pair of the set causes changes in the spectrum, which then requires adjustments in the other pairs. The process turns out to be an iterative one.

Our requirements on the parameter values were first to anchor the isotope-independent peak at 1344 cm^{-1} and then to obtain the best possible shape for the spectrum and also to obtain a distinct isotope dependence for the lower-frequency mode (1130 cm^{-1}). For the host lattice we took the ratio of the lattice beta β_L to the host lattice alpha α_L to be 0.65.[18]

We began by focusing on the high-frequency mode. In order to create the high-frequency iosotope-independent mode, it is necessary to know its origin. Since this mode is dependent only on the presence of nitrogen but not on the nitrogen mass, it is logical to assume that it is due to the vibration of a carbon atom having a very weak interaction with the nitrogen impurity. In our model this has to be the carbon at C(2) in our eight-atom cluster because this atom is furthest from the nitrogen and the most weakly bound.

Therefore, we first assumed a weak carbon nitrogen interaction for this CN pair. As stated earlier, this assumption is supported by the experiments which show the displacement of the nitrogen away from one of the carbon neighbors.[12–14] A simple explanation for this weakened interaction can be formed from the concept of the extra electron that the nitrogen atom provides. In a molecular-orbital picture of the CN molecule this electron would participate in an antibonding orbital which has the effect of weakening the CN bond. In our case, this weakening of the C—N bond relative to the normal lattice C—C bond also leads to a separation of the two atoms which then brings each closer to its other nearest (carbon) neighbors resulting in a strengthening of those bonds. The decoupling of the carbon at C(2) from the nitrogen was accomplished by reducing the central force constant between those two sites to $0.70\alpha_L$.

Further, this mode is outside the main band of the diamond lattice which led us to increase the central force interaction between this carbon at C(2), and its three equivalent carbon neighbors beyond the value used for the host lattice. This is consistent with the picture of this carbon atom being closer to its carbon neighbors here than in the unperturbed lattice. Our previous work[11] yielded a value of $1.35\alpha_L$ and here the final value was $1.40\alpha_L$.

The site-dependent LDOS curves for the different isotopes clearly show the origins of the high-frequency isotope-independent mode. It can be seen that this peak appears only in the site LDOS curves for site C(2) (Fig. 6) and those of the three neighboring carbon sites (Figs. 7 and 8) but it does not appear in the site LDOS for the nitrogen site or in those of its nearest neighbors as can be seen in Figs. 3–5. The isotope independence can be seen by comparing these curves with the corresponding curves for the nitrogen isotope ^{15}N. The figures show the curves to be identical in the vicinity of this mode.

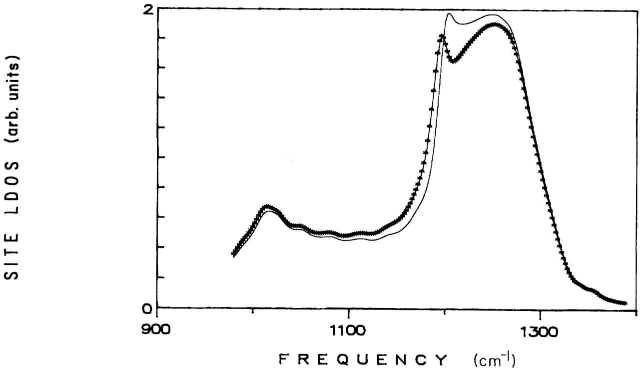

FIG. 4. Local DOS for C(3) along the x direction. The solid curve is for ^{14}N, the other is for ^{15}N.

The mass dependence of the low-frequency mode can be seen from the site LDOS curves for the nitrogen site, Fig. 3, and those of its equivalent neighbors as represented by C(3), Figs. 4 and 5, which clearly show a prominent peak at about 1200 cm^{-1}. Comparison with the corresponding curves for ^{15}N show the isotope dependence of this mode.

Thus, it may seem that the calculation is complete. The two modes of interest have been obtained as well as the correct shape of the total spectrum.[11] However, a problem arises in that the site LDOS curves for the carbon atom at C(2) and its neighbors in our cluster, Figs. 6–8, also show strong isotope-independent peaks in the same region of the spectrum as the isotope-dependent modes (1200 cm^{-1}). These modes, because of their strength, can mask the isotope-dependent mode when the total LDOS is formed. Dealing only with the site-dependent LDOS curves, we found values for the interactions which gave the best fit to the experimental curve for ^{14}N. However, when a total LDOS was constructed for ^{15}N later, the isotope dependence of the low-frequency mode was not reproduced.

The reason can be seen by examining the site LDOS

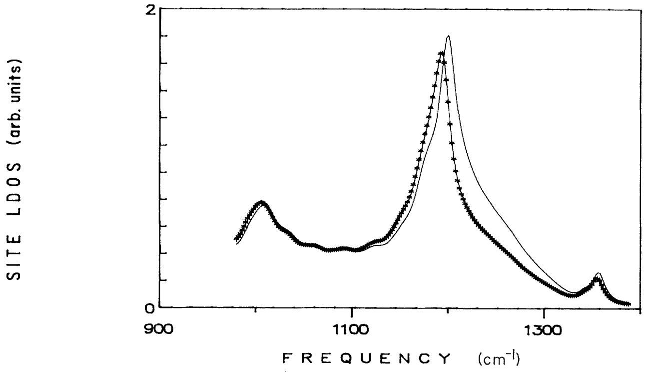

FIG. 3. Local DOS at the nitrogen site along the x direction. The solid curve is for ^{14}N, the other is for ^{15}N.

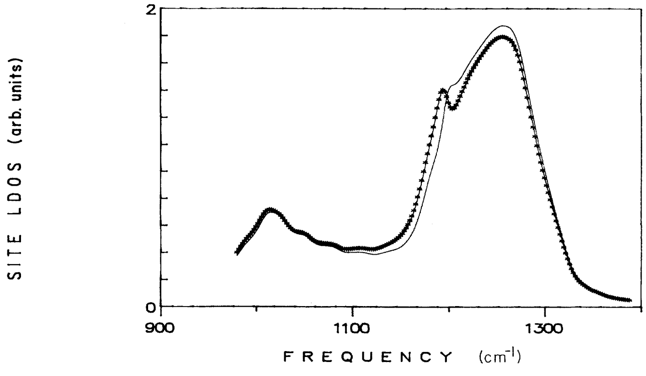

FIG. 5. Local DOS for site C(3) along the z direction. The solid curve is for ^{14}N, the other is for ^{15}N.

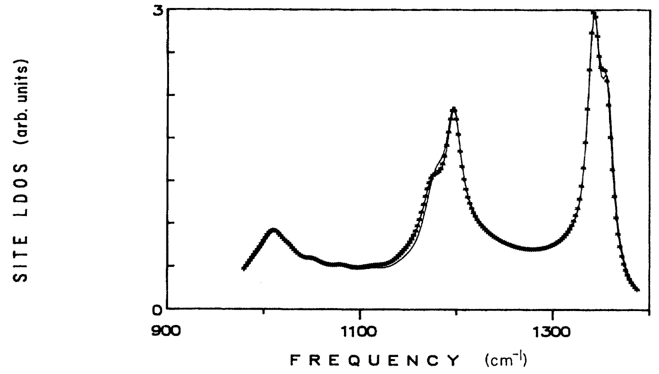

FIG. 6. Local DOS for site C(2) along the x direction. The solid curve is for ^{14}N, the lower is for ^{15}N. The two curves are essentially identical.

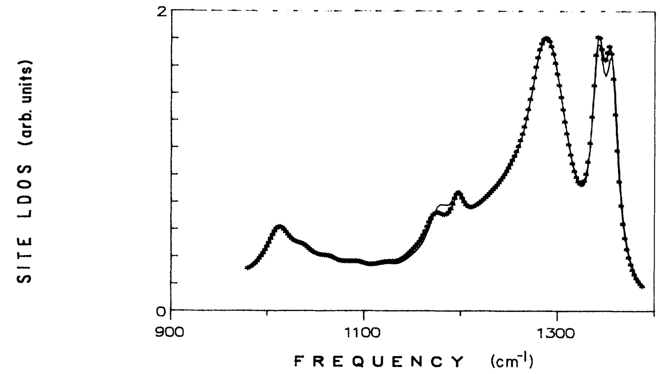

FIG. 8. Local DOS for site C(6) along the z direction. The solid curve is for ^{14}N, the other is for ^{15}N. The two curves are essentially identical.

curves and Eq. (3), which gives the total density of states. The site LDOS curves show that there is a prominent low-frequency mode arising from the nitrogen site at 1200 cm^{-1}, the C(2) site at 1197 cm^{-1}, the C(3) site at 1204 cm^{-1}, and the C(6) site at 1198 cm^{-1}. The C(3) site is one of the three equivalent carbon neighbors of the nitrogen atom and C(6) is the equivalent neighbor site of the CN carbon at C(2). If the mass of the nitrogen is changed we find that the peak shifts 8 cm^{-1} in the nitrogen site and C(3) site LDOS curves but remains at the same frequency, 1198 cm^{-1}, in the C(2) and C(6) carbon site LDOS's.

When the total LDOS curve is constructed, the isotope dependence will disappear unless extra care is taken. The reason can be understood if we consider Eq. (3) which constructs the total LDOS from the site LDOS's. There we see that the weighting factor for the contributing carbon terms, $\rho_x(\mathrm{C}(6))$ and $\rho_x(\mathrm{C}(3))$ is twice that of the nitrogen site, $\rho_x(\mathrm{N})$. Thus, a strong carbon-dependent peak will dominate over a weaker nitrogen peak, which is what happened. What had to be done was to put the nitrogen-14-based peak on the high-frequency side of the carbon peaks. We found that the only way to separate the nitrogen mode from the carbon modes was to increase the central force interaction between the carbon at C(2) and its nearest carbon neighbors and also that of the nitrogen and its three equivalent carbon neighbors beyond its previous values.[11] Additionally, in making the adjustments, care had to be taken regarding the resulting peak intensities of the different contributions because of the weighting factors in Eq. (3). Because of this, we found that by locating the isotope-independent peak due to $\rho_x(\mathrm{C}(6))$ at a slightly lower frequency (1198 cm^{-1}) than that due to the $\rho_x(\mathrm{C}(3))$ peak (1204 cm^{-1}) by adjusting the appropriate α values, we recovered the isotope dependence of the low-frequency mode in the total density of states as shown in Fig. 9. During all these processes the values of the noncentral-force-constant parameter β had to be adjusted to maintain the appropriate shape of the spectrum. This in turn limited the values that could be used for the central-force-constant parameters.

The final values for the different parameters are recorded in Table I. The weakening of the bond between the nitrogen and the carbon at C(2) relative to the lattice values as required by our model is reflected by the values of $0.70\alpha_L$ for the central force constant and an equal weakening of the noncentral value from $0.65\alpha_L$ to $0.45\alpha_L$.

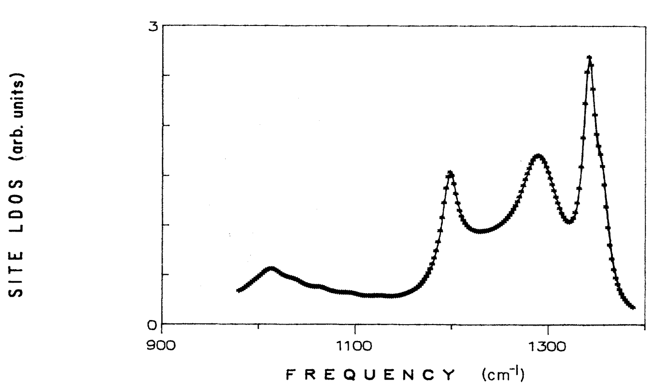

FIG. 7. Local DOS for site C(6) along the x direction. The curves for ^{14}N and ^{15}N are essentially identical.

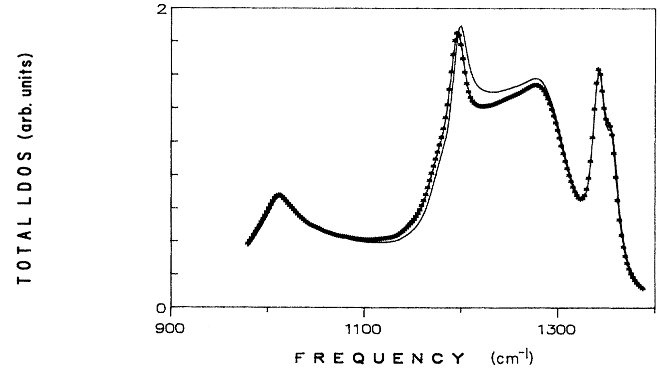

FIG. 9. The total local density of states for isolated nitrogen impurities in diamond. The solid curve is for ^{14}N, the other is for ^{15}N.

TABLE I. Values for the interaction parameters in terms of the host lattice α_L.

Interaction	α	β
Host	1.00	0.65
N-C(2)	0.70	0.45
N-C(3)	1.06	0.61
C2-C(6)	1.40	0.30

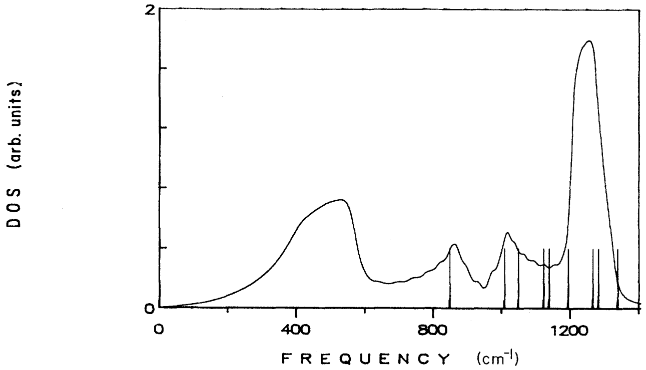

FIG. 10. The local density of states for the diamond lattice in the nearest-neighbor approximation with $\beta/\alpha = 0.65$ (solid line). Vertical lines are one-phonon experimental absorption data taken from Refs. 20 and 21.

The increase in the central force interactions between nitrogen and its three equivalent carbon neighbors is indicative of the physical shift of the nitrogen toward those atoms. The increase in central bonding between the C(2) carbon and its three carbon neighbors results from that carbon having been displaced toward its carbon neighbors as a result of the weakened bond with the nitrogen atom. The reduction of the noncentral force constant β may be attributed in part to the circumstance that there are now only three neighboring bonds in our model instead of four as in the unperturbed lattice.

The final total LDOS for both nitrogen isotopes is shown in Fig. 9. The isotope dependence of the low-frequency mode and the isotope independence of the high-frequency mode are clearly shown.

However, the location of the low-frequency mode is higher than the experimental value by 7%. It was not possible to place it at the experimental value and still maintain the proper shape and obtain the correct isotope behavior for the total spectrum. For example, values for the central force constant less than the final values result in the iosotope dependence being masked regardless of the β values used. Since the low-frequency mode is a resonance mode, its location will be affected by the host lattice and not just the immediate neighborhood. It is known[19] that nearest-neighbor interactions do not give a good representation of the bulk diamond phonon spectrum, especially in this region. Figure 10 shows the bulk phonon DOS for diamond calculated in the nearest-neighbor approximation using $\beta/\alpha = 0.65$ together with the infrared absorption lines.[20,21] It can be seen that in the region in question, while a one-to-one correspondence can be made, the matching is not exact. Therefore, it is not surprising that we could not recover the location of this mode to an accuracy of better than 7%.

SUMMARY

The effect of isolated nitrogen impurities on the phonon spectrum of synthetic diamond has been explained by using a model in which the presence of nitrogen results in an eight-atom cluster which interacts with the host lattice. We were able to obtain the correct shape for the spectrum and locate the two impurity modes of interest. Further, we were able to explain the sources of the two modes and explain the unusual isotope dependence. Lastly, we have demonstrated that focusing attention only on the isolated impurity without consideration of the effects of that impurity on the immediately vicinity will not provide a complete picture of its effects on the properties of the system.

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