First-Principles Calculations of Pseudolocal Vibrational Modes: The Case of Cu and Cu Pairs in Si

S. K. Estreicher* and D. West
Physics Department, Texas Tech University, Lubbock, Texas 79409-1051

J. Goss
Department of Natural Sciences, University of Newcastle, Newcastle upon Tyne NE1 7RU, United Kingdom

S. Knack and J. Weber
Institut für Tieftemperaturphysik, Technische Universität Dresden, 01062 Dresden, Germany
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Pseudolocal vibrational modes (pLVMs) are defect-related vibrational modes which are localized despite being below the phonon maximum. Such modes are sometimes seen as phonon replicas in photoluminescence spectra. The pLVMs associated with two copper-related defects are calculated from first-principles density-functional theory in periodic supercells. The localization of the pLVMs is quantified using the magnitude of the eigenvectors of the dynamical matrix.

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Vibrational mode spectroscopy is a most useful tool to identify impurities in semiconductors. Raman and Fourier transform infrared absorption (FTIR) spectroscopies are commonly used to investigate the local vibrational modes (LVMs) of H, O, and other impurities with mass smaller than that of the host atoms. The identification of the species is obtained from isotope substitutions, uniaxial stress experiments provide the symmetry, and thermal anneals give binding energies. First-principles theory routinely predicts LVMs. In most cases, the curvature of the potential is obtained from total energies calculated for various positions of the light atom around its equilibrium site. For the stretch (wag) mode of Si-H, for example, this involves displacing H along (perpendicular to) the Si-H direction. The accuracy is of the order of 5%–8%. Note that the LVMs relevant to the identification of such impurities are *above* the highest normal mode of the crystal, the Gamma (Γ) phonon.

The situation is more complicated when dealing with defect-related *pseudolocal* vibrational modes (pLVMs), which are localized modes *below* the Γ phonon. Such modes would be difficult to detect by Raman or FTIR but sometimes appear as phonon sidebands (or "replicas") on the low- or high-energy side of the zero-phonon line (ZPL) in photoluminescence (PL) spectra. Which atomic displacements are involved in the pLVMs is not known. Therefore, displacing a few atoms by hand to map the potential surface does not work. Such modes have never been calculated from first principles.

A recently developed method [1] based on perturbation theory allows the computation of all the (harmonic) normal modes of a supercell without physically displacing the atoms. The elements of the dynamical matrix are calculated from the derivates of the density matrix relative to atomic coordinates. The geometry of the system needs to be converged until the largest force component is below 0.005 eV/Å [2]. Large basis sets must be used in order for the density matrix to be accurate. The eigenvalues of the dynamical matrix are the normal modes and the eigenvectors give the relative displacements of the atoms for each mode. The calculation [1] of some 70 known LVMs in Si demonstrated that the error in the frequencies relative to experiment is below 2% on the average. Highly harmonic modes are within 1% and softer modes (such as wag modes) within 3%–4% from the measured ones.

In this work, we use this approach to calculate dynamical matrices, predict pLVMs for Cu-related defects in Si, and quantify the "localization" of these modes. Our molecular-dynamics simulations are based on density-functional theory within the local density approximation (SIESTA [3,4]). The exchange-correlation potential is that of Ceperley-Adler [5] as parametrized by Perdew and Zunger [6]. Norm-conserving pseudopotentials in the Kleinman-Bylander form [7] are used to remove the core electrons from the calculations. The Cu pseudopotential includes relativistic corrections. The basis sets for the valence states are linear combinations of (numerical) atomic orbitals of the Sankey type [8,9] but generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states [3]. Double-zeta plus polarization basis sets are used (for Si: two sets of valence s and p plus one set of d). The charge density is projected on a real-space grid with an equivalent cutoff of 150 Ry to calculate the exchange-correlation and Hartree potentials. This large cutoff is needed to describe the localized d states of copper. Tests from 50 to 250 Ry confirm that this cutoff is sufficient. As in Ref. [1], the $\vec{k}$-point sampling is limited to $k = 0$.

The dynamical matrix in the 128 cell contains 384 normal modes, including three translational modes. This is a far cry from the $\sim 10^{22}$ modes present in the

measured phonon density of states. As the cell is too small to accommodate long wavelength phonons, the ω^2 behavior at low frequencies is not present (the lowest-frequency phonon is around 80 cm^{-1}). The Γ phonon is at 535 cm^{-1}, very close to the 524 cm^{-1} measured [10] at 8 K. Its eigenvector shows that the atomic displacements correspond to the Si-Si stretch along the trigonal axis, as expected.

These calculations can be extended to the calculation of pLVMs. Two examples of such modes are shown in Fig. 1. The PL bands of two Cu-related centers in Si show sidebands separated by 7.05 and 6.42 meV (57 and 52 cm^{-1}), respectively. The bands correspond to distinct defects but the sidebands are sharp and very similar. Note that this type of defect behavior is not unique to copper. Almost all known transition metal PL centers show low-lying pLVMs [11], none of which have been identified.

The defect labeled "Cu_0" (Fig. 1, top), first reported over 30 years ago [12,13], is a trigonal center which contains two copper atoms. It has been identified as the substitutional/interstitial pair [14] $\{Cu_s, Cu_i\}$. The ZPL is at 1014 meV and its deep-level transient spectroscopy (DLTS) level [15] at $E_v + 0.100$ eV. Very weak additional phonon replicas at 16.4 and 25.1 meV (132 and 202 cm^{-1}, respectively) have also been reported [16] in this PL

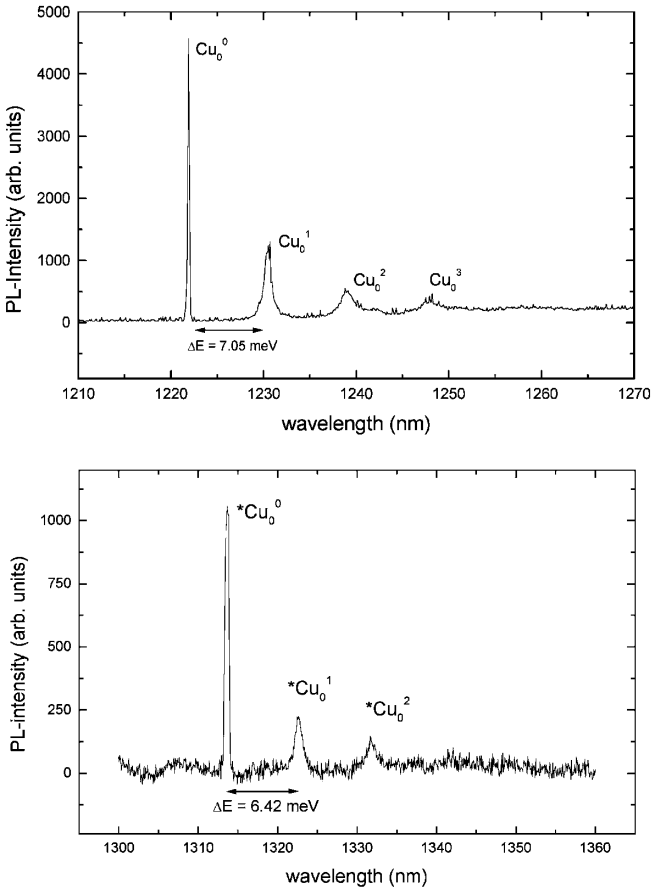

FIG. 1. PL spectra of Cu_0 (top) and $^*Cu_0$ (bottom).

spectrum. Isolated bond-centered (BC) copper has been proposed [17] for it, but our calculations show that the BC configuration is *not* stable. If Cu_i is placed at a relaxed BC site, conjugate gradient calculations drive it out of the BC site to the tetrahedral interstitial (T) site, and the perturbed Si-Si bond is fully restored. There is simply not enough space in Si for Cu_{BC}. The only configuration of Cu_i^0 or Cu_i^+ in Si is at the T site.

The defect labeled "$^*Cu_0$" (Fig. 1, bottom) has a ZPL at 944 meV. It is seen in samples with low copper concentrations [18], in samples annealed at high temperatures [14,19], and in dislocated samples [14]. Uniaxial stress and Zeeman splitting studies [20] suggest T-to-A transitions in T_d symmetry. The authors tentatively proposed [20] that $^*Cu_0$ is isolated Cu_i^+ at the T site. However, these uniaxial stress studies have yet to be repeated at higher stress values. The 944 meV band appears to be associated with a DLTS level at $E_v + 0.185$ eV [14].

Three Cu pairs in Si have been calculated [21]. The $\{Cu_s, Cu_i\}$ pair has Cu_s at a virtually undistorted substitutional site and Cu_i just off the T site, slightly displaced toward Cu_s. The Cu-Cu bond length, 2.273 Å, is within ~0.1 Å of the Si-Si one. The binding energy (calculated with a $2 \times 2 \times 2$ Monkhorst-Pack mesh [22]) is 1.16 eV, close to the measured [23] 1.02 ± 0.07 eV. A second copper pair results from the trapping of a (preexisting) vacancy: $\{Cu_s, Cu_i\} + V \rightarrow \{Cu_s, Cu_s\} + 2.26$ eV. The two coppers are at adjacent substitutional sites with virtually no local distortion. The Cu-Cu separation is 2.283 Å. Note that the reaction $Cu_i + V \rightarrow Cu_s$, where V is a preexisting vacancy, releases 2.78 eV. The third copper pair is 0.22 eV higher than $\{Cu_s, Cu_s\}$ and has orthorhombic symmetry, with the copper atoms at second-nearest substitutional sites. This third pair is not very distinct from two isolated Cu_s impurities. Room-temperature molecular-dynamics simulations of $\{Cu_s, Cu_i\}$ plus V at various locations in the same cell often produce $\{Cu_s, Cu_s\}$ and sometimes $\{Cu_s, Si, Cu_s\}$.

The dynamical matrix of $\{Cu_s, Cu_i\}$ has been obtained in the 64 cell, and those of $\{Cu_s, Cu_s\}$ and of the perfect cell were calculated in the 64 and 128 cells to establish size effects. Comparisons of the modes in the two cells show that the key features are very similar, although better defined in the larger cell.

There are four pLVMs associated with each pair. In the 64 cell, the lowest-lying pLVM is at 73 cm^{-1} for $\{Cu_s, Cu_i\}$ and at 76 cm^{-1} for $\{Cu_s, Cu_s\}$. In this mode, the two Cu atoms move along the trigonal axis *together*. This motion preserves the Cu-Cu bond length. There are two twofold degenerate E modes at 108 cm^{-1} for $\{Cu_s, Cu_i\}$ and 104 cm^{-1} for $\{Cu_s, Cu_s\}$. The Cu atoms move perpendicular to each other in the {111} plane. The highest-frequency pLVM has the two coppers moving against each other along the trigonal axis. This mode is at 282 cm^{-1} for $\{Cu_s, Cu_i\}$ and at 251 cm^{-1} for $\{Cu_s, Cu_s\}$. As for $\{Cu_s, Cu_s\}$ in the 128-atom cell, these modes are at 68, 104, and 263 cm^{-1}, respectively. The lowest pLVM in

both pairs is close to the observed phonon replicas, while the other modes have much higher frequencies.

A measure of the localization of pLVMs can be extracted from the (normalized) eigenvectors of the dynamical matrix. They give the relative direction and magnitude of the displacement of all the atoms in the cell for each vibrational mode. For a pLVM, the displacements are limited to a small number of atoms. Figure 2 shows the total amplitude associated with the two Cu atoms in $\{Cu_s, Cu_s\}$ in the 64 and 128 cells as a function of the frequency. An amplitude of 1.0 would imply that the two Cu atoms move but no Si atoms do. An amplitude of 0.0 would mean that the two Cu remain immobile and only Si atoms move.

Figure 2 shows that the localization varies somewhat with cell size. We expect that it would vary as well if anharmonic contributions could be included. However, the four pLVMs described above clearly exhibit a high degree of localization. For the 68 cm^{-1} mode in the 128 cell, over 70% of the displacements of all the atoms

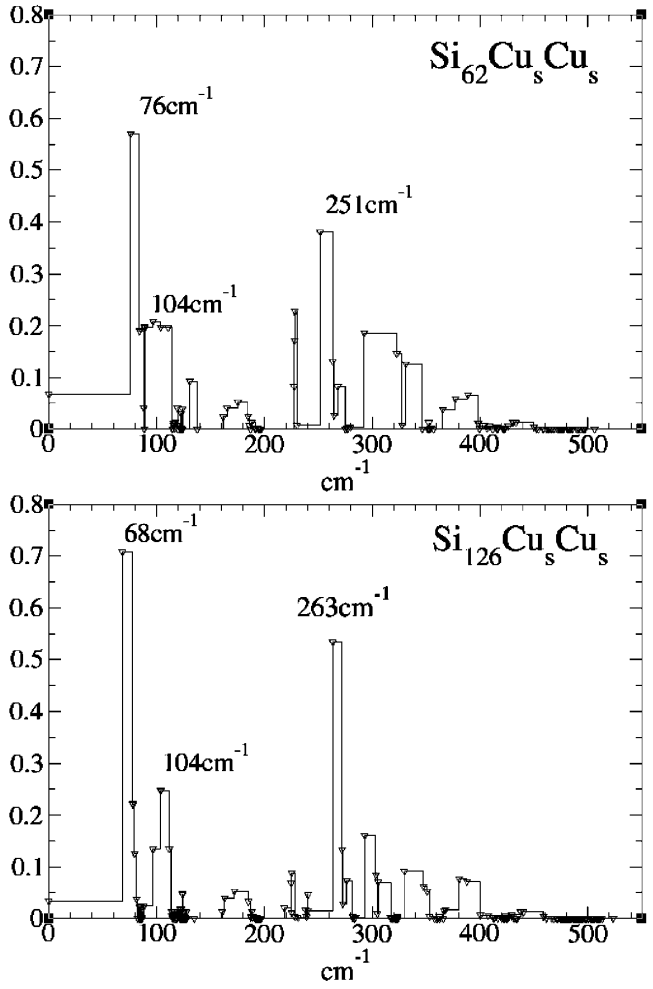

FIG. 2. Localization of the pLVMs associated with the $\{Cu_s, Cu_s\}$ pair in the 64 (top) and 128 (bottom) cells is estimated from the magnitude of the relative displacement of the two Cu atoms, plotted vs the frequency (see text).

involves the two copper atoms. This fraction is over 50% for the 263 cm^{-1} mode and about 30% for the wag modes. A comparison of the 64 and 128 cells shows that the localization is more strongly defined in the larger cell, even though it includes more phonons. In the case of $\{Cu_s, Cu_i\}$ in the 64 cell, the corresponding fractions are about 50%, 30%, and 30%. On the other hand, the orthorhombic $\{Cu_s, Si, Cu_s\}$ pair (in the 64 cell) has no Cu-related mode with more than 20% localization. Thus, some Cu-related modes are highly localized and others are not. As mentioned above, there are no phonons below 80 cm^{-1} in our cells. This could artificially enhance the localization. However, as shown by the mode near 260 cm^{-1}, nearby phonons do not necessarily inhibit localization.

For a local mode to couple to the electronic transition, the direct product of the irreducible representations of the mode, the electronic ground and excited states with that of the dipole operator must contain the fully symmetric representation of the point group.[24] Typically, this restricts the symmetry of the local mode to the fully symmetric representation unless one (or both) of the electronic states is orbitally degenerate.

The $\{Cu_s, Cu_i\}$ pair has C_{3v} symmetry, and the 73 cm^{-1} mode transforms as A_1. It is therefore a strong candidate to couple to the electronic transition. The degenerate E (wag) modes at 108 cm^{-1} do not necessarily couple. The mode at 282 cm^{-1} is A_1 and should show up in the PL band. However, it is close to the weak and broad fourth phonon replica of the 73 cm^{-1} mode. The PL band (Fig. 1, top) has been experimentally identified as the $\{Cu_s, Cu_i\}$ pair. Our calculated symmetry and binding energy agree with experiment, and we find one mode with the appropriate symmetry and frequency, consistent with the phonon replicas. Thus, all the key features of this complex are reproduced.

The $\{Cu_s, Cu_s\}$ pair has D_{3d} symmetry and the 76 cm^{-1} (68 cm^{-1} in the 128 cell) is an A_{2u} mode, *odd* with respect to the inversion symmetry. According to the selection rule, only inversionally even modes can couple to the PL. The wag modes at 104 cm^{-1} (in both cells) are also excluded. The A_{1g} mode at 251 cm^{-1} (263 cm^{-1} in the 128 cell) could couple, but it is too high to generate the observed replicas. Thus, $\{Cu_s, Cu_s\}$ is unlikely to be the $^*Cu_0$ center. This pair is also inconsistent with the reported T_d symmetry [20], even though experiments with higher stress values are needed to confirm these data.

Note that theory cannot completely rule out that $\{Cu_s, Cu_s\}$ is $^*Cu_0$. (i) There could be *several nearby excited states*, *gerade* and *ungerade*. The Cu-Cu bond includes a (*gerade*) σ-bond contribution from the $4s$-$4s$ overlap as well as (*ungerade*) π-bond contributions involving the $3d_{yz}$ and $3d_{zx}$ orbitals. These have g and u antibonding orbitals. If the excited electron goes sometimes into one, sometimes into another, one could see both the ZPL and the phonon replicas. (ii) The population analysis shows that the highest-occupied orbital is a

singlet but the lowest-unoccupied orbitals are a pair of doublets. Upon excitation or trapping of an electron, the doublet becomes Jahn-Teller active and the symmetry drops. These two scenarios are unlikely but possible.

What are the other possibilities? $^*Cu_0$ is observed when the copper concentration is low [18], suggesting that $^*Cu_0$ is a precursor of $\{Cu_s, Cu_i\}$. Further, $^*Cu_0$ is seen in samples containing dislocations or annealed at high temperatures [14]. This suggest that traps for copper are available in these samples, again leading to low concentrations of such a precursor. Finally, uniaxial stress experiments [20] suggest that $^*Cu_0$ has T_d symmetry. The precursors of $\{Cu_s, Cu_i\}$ are Cu_i and Cu_s, both of which have T_d symmetry. However, $^*Cu_0$ is not seen by PL in samples in which Cu_s is seen by DLTS, and $^*Cu_0$ appears to be associated with the DLTS peak at $E_v + 0.185$ eV [14] while Cu_i is believed [25] to have a donor level near $E_c - 0.2$ eV. Although its activation energy for diffusion is very low [26,27], Cu_i is not very mobile below 10 K, where the PL data were taken. For completeness, we calculated the dynamical matrices of Cu_s and Cu_i and analyzed the localization of any Cu-related modes.

We find no pLVMs associated with Cu_s with localization stronger than 20%. This is much less than the 70% or so we obtain for the copper pairs discussed above. Cu_i has one threefold degenerate pLVM around 150 cm^{-1} with about 30% localization. This is insufficient to make any convincing statement, but we cannot rule out that isolated interstitial copper could be $^*Cu_0$. More experimental data on this center are needed.

In conclusion, we have presented first-principles calculations of pLVMs associated with copper and Cu pairs in Si. The localization of some of these modes is demonstrated. The calculated properties of the $\{Cu_s, Cu_i\}$ pair include the measured symmetry and binding energy, and the phonon replicas seen by PL are identified. Very similar pLVMs are associated with another trigonal copper pair, $\{Cu_s, Cu_s\}$. However, the pLVM in the right frequency range has A_{2u} symmetry and should not couple to the PL unless some exotic conditions are realized. The analysis of the dynamical matrices of the tetrahedral Cu_s and the orthorhombic $\{Cu_s, Si, Cu_s\}$ complex show that neither exhibits pLVMs with more than ~20% localization. The tetrahedral Cu_i has a T mode with about 30% localization but it is quite high in frequency. More experimental data on $^*Cu_0$ are needed to identify this defect.

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*Electronic address: stefan.estreicher@ttu.edu

[1] J. M. Pruneda, S. K. Estreicher, J. Junquera, J. Ferrer, and P. Ordejón, Phys. Rev. B **65**, 075210 (2002).
[2] This is nearly an order of magnitude smaller than the typical convergence criterium for geometries.
[3] D. Sánchez-Portal, P. Ordejón, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
[4] E. Artacho, D. Sánchez-Portal, P. Ordejón, A. García, and J. M. Soler, Phys. Status Solidi (b) **215**, 809 (1999).
[5] D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).
[6] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[7] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[8] O. F. Sankey and D. J. Niklevski, Phys. Rev. B **40**, 3979 (1989); O. F. Sankey, D. J. Niklevski, D. A. Drabold, and J. D. Dow, Phys. Rev. B **41**, 12750 (1990).
[9] A. A. Demkov, J. Ortega, O. F. Sankey, and M. P. Grumbach, Phys. Rev. B **52**, 1618 (1995).
[10] J. Menéndez and M. Cardona, Phys. Rev. B **29**, 2051 (1984).
[11] H. Conzelmann, Appl. Phys. A **42**, 1 (1987).
[12] N. S. Minaev, A. V. Mudryi, and V. D. Tkachev, Sov. Phys. Semicond. **13**, 233 (1979).
[13] J. Weber, H. Bauch, and R. Sauer, Phys. Rev. B **25**, 7688 (1982).
[14] S. Knack, J. Weber, H. Lemke, and H. Riemann, Physica (Amsterdam) **308B–310B**, 404 (2001).
[15] H. B. Erzgräber and K. Schmaltz, J. Appl. Phys. **78**, 4066 (1995).
[16] S. P. Watkins, U. O. Ziemelis, M. L. W. Thewalt, and R. R. Parsons, Solid State Commun. **43**, 687 (1982).
[17] M. Nakamura, S. Ishiwari, and A. Tanaka, Appl. Phys. Lett. **73**, 2325 (1998); M. Nakamura, Appl. Phys. Lett. **73**, 3896 (1998); **79**, 2904 (2001).
[18] K. G. McGuigan, M. O. Henry, E. C. Lightowlers, A. G. Steele, and M. L. W. Thewalt, Solid State Commun. **68**, 7 (1988).
[19] S. L. Pinjare, N. Balasubramanyam, and V. Kumar, Phys. Status Solidi (a) **113**, K261 (1989).
[20] K. G. McGuigan, M. O. Henry, M. C. Carmo, G. Davies, and E. C. Lightowlers, Mater. Sci. Eng. B **4**, 269 (1989).
[21] S. K. Estreicher, D. West, J. M. Pruneda, S. Knack, and J. Weber, MRS Proc. **719**, 421 (2002).
[22] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[23] A. A. Istratov, H. Hieslmair, T. Heiser, C. Flink, and E. R. Weber, Appl. Phys. Lett. **72**, 474 (1998).
[24] G. Davies, Phys. Rep. **176**, 83 (1989).
[25] C. Flink, H. Feick, S. A. McHugo, A. Mohammed, W. Seifert, H. Hieslmair, T. Heiser, A. A. Istratov, and E. R. Weber, Physica (Amsterdam) **273B–274B**, 437 (1999).
[26] D. E. Woon, D. S. Marynick, and S. K. Estreicher, Phys. Rev. B **45**, 13 383 (1992).
[27] A. A. Istratov, H. Hieslmair, C. Flink, T. Heiser, and E. R. Weber, Phys. Rev. Lett. **81**, 1243 (1998).