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A new structure of Cu complex in Si and its photoluminescence

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Abstract

A recent discovery of complicated isotope shifts of the PL 1014 meV line in Cu-containing silicon, which was made by Thewalt's group, indicates that existing models of Cu pairs are not appropriate for accounting for the luminescence center. A new structural model has been studied. First-principles calculations show that the most probable form of the complex is a four-membered complex which is composed of a substitutional Cu associated with three neighboring interstitial Cu atoms. The symmetry is C_{3v} . The formation mechanism of this complex is discussed.

For interpreting the complicated splitting for the Γ_4 exciton peak, involvement of a non-totally symmetric mode is proposed. The pattern of splitting obtained by this model is almost in agreement with the experiment. Selection rules beyond the usual treatments are necessary to connect a specific exciton peak to the corresponding phonon.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

With increasing use of metal Cu in Si device processes, control of the Cu impurity becomes of emergent importance, because it is a fast diffusive species among various impurities and causes degradation of devices [1, 2]. Normally, Cu atoms enter at a tetrahedral (T) interstitial site [3–5]. The fast diffusivity occurs through jumps from the stable T site to an adjacent T site through a hexagonal site [6–8]. Although there are some arguments stating that the substitutional site is stable [9, 10], the point that the interstitial T site is the most stable one is now undisputable.

However, a small fraction of Cu atoms can enter at the substitutional site [3, 4], and some of them form complexes under some circumstances. These complexes act as electrically and optically active centers. An optical signature of the complex was found in photoluminescence (PL) spectra [11, 12]. Weber *et al* systematically studied the PL spectra [12]. Several emission lines were observed and were attributed to the bound excitons formed around the Cu complex. Among them, the most intense and sharp emission line at 1014 meV, which is denoted as Cu_0^0 , is the issue of the present paper. The sharp line is a characteristic feature

of a zero-phonon (ZP) line. The associated sidebands have equal separations of 7.05 meV and are attributed to the phonon replica with $\omega = 56.8 \text{ cm}^{-1}$. They carefully analyzed this Cu_0^0 line and deduced that this sharp line is actually a composite peak; the involved excitons are Γ_3 and Γ_4 states. The energy separation is so close (0.15 meV) that these two were not resolved in their spectra at that time. The 1014 meV line is well correlated with the so-called DL2 signal in deep-level transient spectroscopy (DLTS), the impurity level being 0.1 eV above the top of the valence band [13]. Accordingly, it is understood that the two signals have the same origin at a Cu complex.

The nature of the Cu complex was known by the analysis of Weber *et al* [12]. By examining uniaxial stress experiments, it has been unambiguously determined that the symmetry of the complex is trigonal. By examining the Cu concentration dependence on the intensity of the Cu_0^0 line, it is inferred that the complex is a pair of Cu. The latter point is, however, an issue which is currently being debated [14–16]. The method of determination of Cu concentration is subjected to Nakamura's criticism because of the fast diffusion. Despite this criticism, the pair model seemed to be widely accepted. Theoretical studies by Estreicher *et al* [17, 18] support the pair model. The local vibrational mode was also calculated to give frequencies

similar to the experiment. At this point, it seemed that the pair model had been firmly established.

In spite of the well-analyzed feature of the 1014 meV line, it is a surprise to see that a completely different picture came out by a study of Thewalt's group of the isotope shift of the ZP line [19, 20]. By using highly enriched ^{28}Si to eliminate the inhomogeneous isotope broadening [21, 22], they have succeeded in resolving the Γ_3 and Γ_4 peaks of the Cu_0^0 line, and more importantly to show that each peak has fine structure. For the Γ_3 exciton peak, when the natural abundance of Cu (69.09% ^{63}Cu and 30.91% ^{65}Cu) is used, an extra four peaks appear, in addition to the one peak which is observed when an isotopically pure sample is used. This suggests that a complex consists of four Cu atoms. For the Γ_4 exciton peak, a more complicated splitting appears. Three groups of peaks exhibit further splitting; in total 1:3:5:3:1 splitting. Whereas isotope shifts for the ZP line are described in the literature [23, 24, 22] and a detailed description for the ZP line is available [25, 26], the mechanism of this complicated splitting is not known.

By considering the importance of the new result by Thewalt's group, a structural model must be examined for the Cu complex including four-membered complexes. Various forms of the complex are investigated by first-principles calculations. Although Thewalt's group extended their isotope experiment to other impurities [27], here we will focus on the Cu complex only. An important issue is the interpretation of such a complicated splitting of isotope shifts, for which we propose a new model based on phonon properties.

2. Calculation method

The model structures for the Cu complex which were examined in this study range from Cu_2 to Cu_4 . The stable structure was studied by DFT total-energy calculations by using the supercell method. The stability is estimated by the binding energy E_b of Cu atoms. In order to make it meaningful to compare various configurations with different numbers of Cu atoms, the binding energy E_b was evaluated as being measured per impurity atom. For concreteness, the definition of E_b for complex Cu_m should be recorded as

$$E_b(\text{Cu}_m) = \frac{1}{m} [E(\text{Si}_n\text{Cu}_m) - (mE(\text{Si}_n\text{Cu}) - (m-1)E(\text{Si}_n))], \quad (1)$$

where n is the size of the supercell used. In this equation, the reference configuration of Si_nCu is taken to be an interstitial T-site Cu. Although the binding energy is usually defined as being negative of the energy difference (1), we will leave the sign as it was.

The total-energy calculation was performed by the pseudopotential method with LDA. The code used is *Osaka2k* [28]. The norm-conserving pseudopotentials of Troullier–Martins-type are used with the help of the Kleinman–Bylander form [29, 30]. No spin polarization was used. Wavefunctions were expanded with the cutoff energy of 50 Ryd. The Γ point was used for the k -point sampling. For comparing the formation energy of different configurations, these conditions are good enough. Details of the convergence of the calculation is described in our previous paper [31].

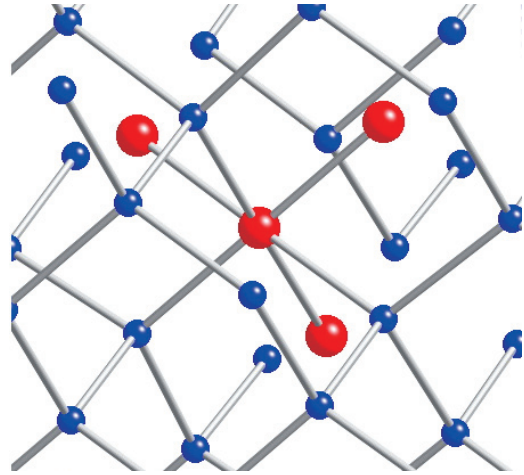


Figure 1. The most stable Cu complex of E type, $\text{Cu}_{(s)}\text{Cu}_{(3i)}$: big and red (light-colored) spheres indicate Cu, while small and blue (thick-colored) ones indicate Si. The substitutional Cu atom has sixfold coordination.

The impurity configurations were modeled by 64-atom supercells. The cell parameters were fixed to the experimental value. Atom positions were optimized by using Hellmann–Feynman forces, until the average residual force become less than typically 1×10^{-3} Ryd/Bohr.

3. The stable configuration

3.1. Results

We have calculated various configurations of Cu complexes. For Cu pairs, four models have been considered. (A) S–I pair consisting of a substitutional Cu associated with the nearest-neighbor T-interstitial Cu. This configuration is what Estreicher found to be the most stable one [17]. (B) Another S–I pair in which Cu pair is more separated, with an Si atom beginning at the intermediate position. This model was included in connection with Estreicher's work [18]. In the undisplaced configurations, both have C_{3v} symmetry, whose symmetry axis is the $\langle 111 \rangle$ direction. (C) S–S pair consisting of two substitutional Cu atoms. This has D_{3d} symmetry. (D) I–I pair consisting of T-interstitial Cu atoms.

For the Cu_4 complex, two configurations are considered. Configuration E, S–3I, consists of one substitutional Cu and three interstitial Cu atoms which are located at antibonding sites. For the undisplaced configuration, it has C_{3v} symmetry. In configuration F, 4I, all Cu atoms are located on the interstitial T sites around a host Si atom. It has T_d symmetry in its original form.

By starting with these positions as the initial guess, the structures were optimized by the conjugate-gradient method. The binding energies E_b of optimized structures are compared in table 1. The strongest bonding is formed in the Cu_4 configuration of type E, that is, $\text{Cu}_{(s)}\text{Cu}_{(3i)}$. The atomic configuration is shown in figure 1. Three $\text{Cu}_{(i)}$ are located at the T-interstitial sites, each being the antibonding (AB) site of the original Si–Si bonds. Hence, three sets of $\text{Cu}_{(i)}$ – $\text{Cu}_{(s)}$ –Si form sixfold coordination around the $\text{Cu}_{(s)}$. The

Table 1. The binding energy E_b of Cu complexes in eV units.

Cu ₂		Cu ₃		Cu ₄		
A	B	C	D	G	E	F
S-I	S-Si-I	S-S	I-I	S-2I	S-3I	4I
-0.91	-0.64	-0.94	-0.89	-0.66	-1.30	-1.02

remaining Si out of four neighboring Si atoms around Cu_(s) moves out from the original position by 3.4%. Hence, the bond between the Si and Cu_s does not appear in figure 1. The next stable configuration is also the Cu₄ configuration of type F, that is, Cu_(4i). This indicates that forming the Cu₄ complex is energetically favorable over forming Cu₂. If a sufficient number of Cu impurities are close enough, it would be easier to form Cu₄ complexes.

For either case, the binding energy of Cu₄ complexes is strong, i.e. more than 1.0 eV. Hence, once a Cu₄ complex is formed, it is quite stable. Indeed, Nakamura demonstrates a characteristic of a long-lived center for the PL 1014 meV line, with the lifetime being longer than two years at room temperature [32]. Among two Cu₄ complexes, configuration E is obviously favorable in terms of the strongest binding energy and of the symmetry C_{3v}, which is consistent with Weber's uniaxial experiment [12].

In the usual sense, configuration F must be rejected for the candidate because of symmetry T_d. However, it seems better not to completely exclude this possibility simply because of symmetry. For isoelectronic centers, where long-range Coulombic forces are lacking, Davies argues that bound excitons sometimes cause lattice distortions; the symmetry appearing in a photoluminescence spectrum could be lowered from the symmetry of the original ground state [33–35]. A model Cu_(4i) composed of interstitial Cu only may have some roles when the forming process of the complex is investigated, which will be described later. Although the possibility of F is noted, we discuss mainly configuration E in most of the remaining paper.

Let us check the atomic configuration of Cu complexes. In table 2, the bond lengths are also listed for selected atomic configurations. One can find a tendency that the substitutional Cu_(s) pulls the nearest-neighboring Si atoms in, while the interstitial Cu_(i) pushes the surrounding atoms away. This tendency is what is found in a single Cu impurity in silicon [31]. In the case of a single Cu, the bond length of Cu_(i) is increased by 2.1%, whereas that of Cu_(s) is decreased by 3.2% on average. It may be interesting to point out that for Cu_(s) Jahn–Teller distortion occurs, from which the symmetry is lowered to D_{2d} [36]. Experimentally, it is reported that Cu_(s) is appreciably displaced from the original substitutional site [9]. This Jahn–Teller distortion of Cu_(s) and its shortening of the bond length seem to be a driving force for attracting extra Cu atoms in its vicinity.

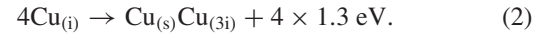
3.2. Discussion

What the present calculation indicates is that the four-membered complex with one substitutional Cu, i.e. Cu_(s)Cu_(3i), is the most stable complex in thermal equilibrium conditions,

Table 2. Bond length of Cu complexes. Relative change in the bond length from the original length 2.35 Å is indicated in the fourth column.

Config.	Bond	Length (Å)	Change (%)	Symmetry
A	Cu _(i) –Si	2.42–2.53	3.0–7.7	—
	Cu _(s) –Si	2.30–2.40	–2.1–2.1	
	Cu _(s) –Si (axial)	2.22	–5.5	
	Cu _(s) –Cu _(i)	2.31	–1.7	
B	Cu _(i) –Si	2.45–2.50	4.3–6.4	—
	Cu _(i) –Si (axial)	2.37	0.85	
	Cu _(s) –Si	2.22–2.31	–5.5 to –1.7	
	Cu _(s) –Si (axial)	2.26	–3.8	
E	Cu _(s) –Cu _(i)	2.34	–0.43	C _{3v}
	Cu _(s) –Si	2.32	–1.3	
	Cu _(s) –Si (axial)	2.43	3.4	
F	Cu _(i) –Si	2.38	1.3	T _d

actually at such a temperature low enough that the entropy contribution does not alter significantly the free energy. The reaction is formulated as



The problem of applying this conclusion in an interpretation of Cu experiments is that in many cases the thermal equilibrium conditions do not hold, because of the ultra-fast diffusivity of Cu; changing temperature causes a non-uniform distribution of Cu atoms [14, 37–39]. The final result depends on the process itself. With this caution in mind, we will discuss formation (or dissociation) of the Cu complex.

First of all, we would like to emphasize that use of the law of mass action is inappropriate for deducing the form of the Cu complex. So far, the argument for deducing the form of the Cu complex has been based on the law of mass action. The concentration dependence on the PL intensity was examined, showing quadratic dependence [12] or linear dependence [14, 16]. One significance of Thewalt's result is showing that neither form is true. Despite the simplicity of reaction (2), it is often the case that many intermediate reactions are involved. Then, no simple dependence of concentration can be expected. There is no guarantee that either the dissociation or formation energy is given by equation (2).

The dissociation energy was obtained by DLTS measurement (DL2 line) to be 1.02 eV by Istratov *et al* [40]. Estreicher *et al* compared their calculated binding energy with this value [17]. However, Nakamura and Iwasaki showed that the dissociation energy obtained by the PL 1014 meV line is different (0.63 eV) from the value obtained by DLTS [15]. Even though both lines had the same origin, the decay rate of these signals may depend on the detailed process of PL emission or carrier trapping. Therefore, the PL 1014 meV line should be the appropriate quantity which is qualified as the reference for the present calculation. Nakamura and Iwasaki showed, in the same paper, that the formation energy of the PL center is 0.57 eV. Obviously, the formation process is different from the dissociation process. The starting states of Cu for which the above experiments were performed may be different from the

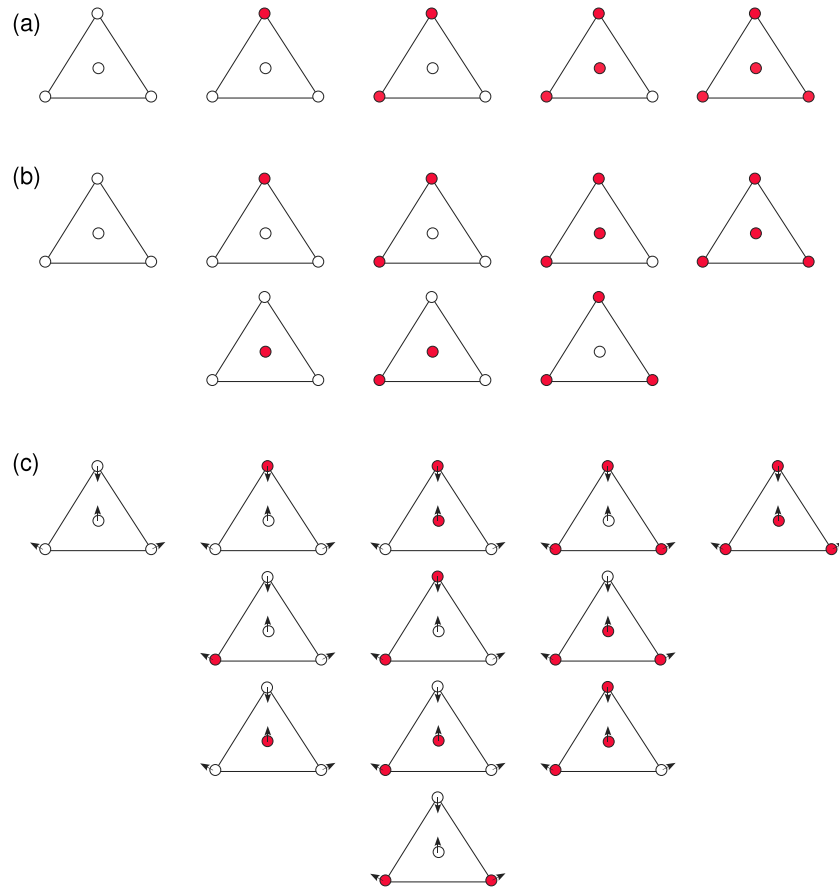


Figure 2. Successive substitution of ^{63}Cu with ^{65}Cu (red or gray circles) in the Cu_4 unit; (a) for an A_4 molecule with T_d symmetry, (b) and (c) AB_3 molecule of C_{3v} symmetry. (a) and (b) Show all the static configurations of inequivalent symmetry. (c) Shows all the distinct vibrations for y-polarized E mode.

left-hand side of reaction (2), so that any listed value in table 1 should not be directly compared with experimental formation or dissociation energy.

A four-membered complex is not at all unusual. It was reported that Li and Br form such complexes [41]. In these cases, however, for example, four Li atoms get together around a vacancy, i.e. Li_4V [42]. This type of complex seems unlikely to occur for Cu. In our previous study of a single Cu impurity [10], the binding energy of $\text{Cu}_{(i)}$ with vacancy V is as large as 3 eV, so that $\text{Cu}_{(i)}$ would immediately replace V to form $\text{Cu}_{(s)}$ if $\text{Cu}_{(i)}$ is close to V. Similar arguments were made by others [43, 44]. Hence, for the present Cu complex, no vacancy must be associated with in thermal equilibrium.

For Cu_4 , it seems likely that first a substitutional $\text{Cu}_{(s)}$ atom is present by some means, and then interstitial $\text{Cu}_{(i)}$ atoms come close together, because of the fast diffusivity. The substitutional $\text{Cu}_{(s)}$ is immobile, so that a complex $\text{Cu}_{(s)}\text{Cu}_{(3i)}$ is too. Then, the question is how substitutional Cu atoms enter silicon. Nakamura [16] argued the impossibility of $\text{Cu}_{(s)}$ of such a level of concentration as 10^{13} cm^{-3} at the temperatures at which their samples were prepared, based on the solubility data by Hall and Racette [3] or Meek and Seidel [4]. This point could be criticized by arguing that the estimation of intrinsic solubility at such a level is an extreme extrapolation from a very high concentration regime ($\sim 10^{19} \text{ cm}^{-3}$), so that

such an extrapolation is unreliable. An interesting experiment was performed by Nakamura *et al* as to whether introducing a vacancy can promote the concentration of $\text{Cu}_{(s)}$ or not [45]. Their result shows that the intensity of the PL 1014 meV line is decreased by introducing a vacancy, and that the intensity is recovered by annealing. From this, they conclude that $\text{Cu}_{(s)}$ is not responsible for the PL 1014 meV line. In this way, there is still some inconsistency and hence the issue as to whether the substitutional Cu is a constituent of the complex or not is left as an open question.

4. Phonons and isotope shifts

4.1. Isotope splitting

The most prominent result of Thewalt's experiment is the complicated splitting of the ZP line due to the Cu isotope. For the Γ_3 exciton peak, a total of five peaks appears when natural abundance Cu is used. This splitting can be easily understood for a four-membered complex, Cu_4 , as shown in figure 2(a). Successive substitution of ^{63}Cu with ^{65}Cu in the Cu_4 unit yields five patterns of configuration $^{63}\text{Cu}_m^{65}\text{Cu}_n$, where $m + n = 4$.

The difficulty is about further fine splitting for the Γ_4 exciton peak; three groups of peaks are further split into three to five subpeaks, namely 1:3:5:3:1. Such a complicated

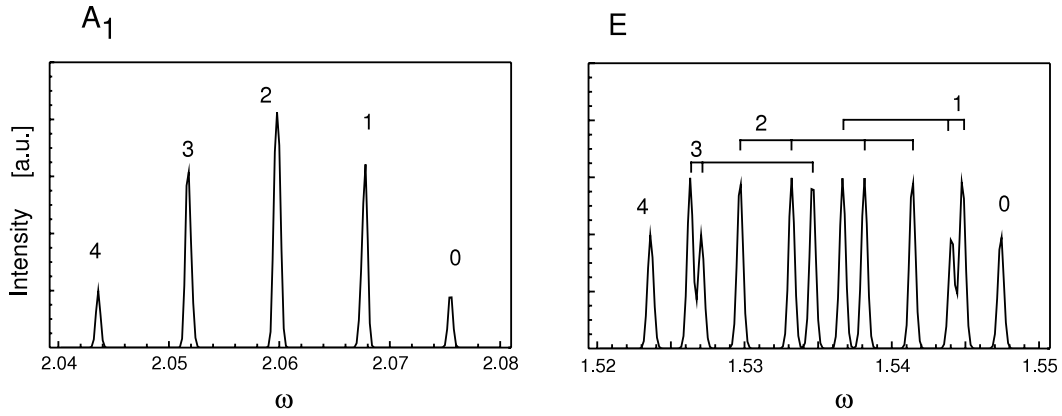


Figure 3. The isotope shift of the vibrations due to successive substitution of the mass M_0 with a mass M_1 . The number of atoms with mass M_1 is indicated in the spectra. An AB_3 -type molecule, which is slightly distorted from T_d symmetry, is used. The frequency ω is expressed in $(f_r/M_0)^{1/2}$ units. For the mass ratio of isotopes, $M_1/M_0 = 65/63$ is used. The other parameters are as follows: $f_r = 1.0$, $f_{r1} = 1.05$ and $f_a = f_{a1} = 0.01$. The line spectra are plotted with Gaussian broadening.

splitting is observed only for Cu among a series of similar experiments [27].

This kind of complicated splitting is not observed for the first time. In Li-doped silicon, where similar splitting due to isotope substitution was found [41, 24]. For the Li_4 complex, two types of splitting was found. The splitting of the Q_L line seems the same as that of Γ_3 for the Cu complex, namely five peaks. The splitting of the Q line looks like that of Γ_4 for the Cu complex, but the number of subpeaks is different, 1:2:3:2:1. For the Li_4 case, both exciton peaks are attributed to a transition Γ_3 to Γ_1 in C_{3v} symmetry; Q corresponds to a spin triplet while Q_L to a spin singlet [46]. Canham *et al* interpreted the subsplitting of Q in terms of lowering symmetry to C_{3v} in atomic configurations. In C_{3v} , the numbers of different ways of arranging two kinds of isotopes are 1:2:2:2:1, as shown in figure 2(b). This interpretation is almost satisfactory for the subpeaks of Q , except the number of the third group is different only by one.

Attention thus far has been paid to the number of ways of static configurations. When non-totally symmetric vibrations are taken into account, the number of ways can be increased. This is illustrated in figure 2(c), by taking the y -polarized component of the E mode of a molecule with C_{3v} symmetry as an example. For example, for one substitution ^{65}Cu in C_{3v} , although there are only two different ways in the static configurations, atomic displacements make some of the symmetry-equivalent configurations different dynamically, leading to three distinct frequencies. For a y -polarized component of E mode, we thus have 1:3:4:3:1 splitting, which is close to the situation of the Γ_4 exciton. For the E mode, there is yet another component, that is, of x polarization. It is not quite obvious that double degeneracy of the E mode means simply duplication of the splitting pattern for the y -polarized component. Hence we examined phonon calculations by using a simple model of the AB_3 molecule with C_{3v} symmetry, which is composed of the same species.

The vibrations are calculated by a valence-force model with two bond-stretching force constants (f_r and f_{r1}) and two angle force constants (f_a and f_{a1}), where 1 refers to that of

the apex atom. The result is shown in figure 3. The line spectra are plotted with Gaussian broadening. We see again 1:3:4:3:1 splitting, but with different weighting. Although we are still missing one subpeak for the third group, the result seems almost satisfactory. If we render the AB_3 molecule close enough to tetrahedral symmetry, the E mode becomes a part of the triply degenerate mode T. Then more peaks due to the other partner A_2 appear around this region. Note that even for the totally symmetric mode A_1 , there must be two subpeaks for the second, third and fourth groups, as expected in figure 2(b). The appearance of five peaks in figure 3 is just because the splitting is not large enough to be resolved. In the experimental spectra of the Γ_3 exciton [19], the second peak seems to have two subpeaks.

In this way, it seems pertinent to interpret that the Γ_3 exciton is associated with the A_1 phonon and the Γ_4 exciton with the E phonon. If the deviation from T_d is only slight, the Γ_4 exciton may be associated with the T phonon. Local vibrations were obtained by first-principles phonon calculations. There are several Cu-related phonons with low frequency. The details of eigenvectors and their symmetry will be given in our conference proceeding [47].

4.2. Selection rules

The foregoing argument requires that a specific exciton is coupled to a specific phonon mode. This suggests that there must be some selection rules between electronic and phonon parts, most likely due to symmetry. In general such selection rules, of course, must be present.

In optical spectra, one observes transitions from an initial state $|kn\rangle$ to a final state $|ln'\rangle$, where kl is the label of the electronic part $\psi_k(\mathbf{r})$ and nn' is that of the phonon part $\chi_n(\mathbf{R})$. The transition rate is determined by the matrix element $P_{km}(Q)$ of the dipole transition [48]

$$\langle kn|\hat{P}|ln'\rangle = \int dQ P_{km}(Q)\chi_n^k(Q)^*\chi_{n'}^m(Q) \quad (3)$$

where

$$P_{km}(Q) = \int d\mathbf{r} \psi_k^*(\mathbf{r}, Q) P \psi_m(\mathbf{r}, Q) \quad (4)$$

is the matrix element of the electronic part including the phonon coordinate Q as a parameter. Formally, for the transition matrix elements $\langle kn|\hat{P}|mn'\rangle$, there are selection rules due to symmetry, which are determined by a standard technique of the group-theoretical method. However, such formal selection rules at this level are rarely used in interpretation of PL spectra.

In practice, because of very different masses of electrons and ions, approximations of different levels are used, depending on the extent to which the electronic part and phonon part can be separated. Within the Franck–Condon approximation, the shape function $F(\omega)$ is given by

$$F(\omega) = \sum_n \rho_{k,n} \times \int dQ |P_{km}(Q)|^2 |\chi_n(Q)|^2 \delta(\omega - U_m(Q) + E_{k,n}). \quad (5)$$

By smearing the dependence of P_{km} on Q out, one obtains

$$F(\omega) = |P_{km}|^2 A \int dQ |\chi_n(Q)|^2. \quad (6)$$

This is the Condon approximation, where the electronic part and vibronic part are completely decoupled. In discussing the lineshape for the ZP line, this Condon approximation is frequently used [25, 48]. This treatment is obviously not appropriate for the present Cu complex. We should come back to the original matrix elements (3).

For the ZP line, a transition for the phonon part is represented by $|0\rangle \rightarrow |0\rangle$. The zero-point motion has totally symmetric Γ_1 , irrespective of which symmetry the phonon mode possesses [49]. All transitions of the phonon part are allowed by symmetry alone. Therefore, the symmetry of the matrix element $\langle k0|\hat{P}|m0\rangle$ is determined solely by that of the electronic part P_{km} . The electronic part $P_{km}(Q)$ still possesses the phonon contribution through the parameter. It is often the case that the matrix element $P_{km}(Q)$ is evaluated at $Q = 0$, then the electronic part and phonon part are completely decoupled. Therefore, for the present problem, it must be essential to consider the matrix element $P_{km}(Q)$ at displaced configurations, i.e. $Q \neq 0$, and hence $\psi_k(\mathbf{r}, Q)$ for $Q \neq 0$ must be used. The authors suggest investigating the selection rules from this point of view.

5. Conclusion

We have studied the complicated isotope shift of the PL Cu_0^0 line, which was discovered by Thewalt's group. The most probable form of the Cu complex is a four-membered complex of type $\text{Cu}_{(s)}\text{Cu}_{(3i)}$ with C_{3v} symmetry, in terms of the binding energy. However, the binding energy is not the absolute measure of the stability for the complex in the real situation. Depending on the starting state of the Cu impurity, the formation energy is more important, and has not been determined in this study alone. In this case, we cannot exclude a complex model $\text{Cu}_{(4i)}$.

For the complicated splitting for the Γ_4 exciton, a suitable interpretation is that a non-totally symmetric mode like the E mode is associated with the zero-phonon peak. Study of the actual frequency and its symmetry by *ab initio* phonon calculations is in progress.

Acknowledgments

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