I. INTRODUCTION

An isotope shift of sharp zero-phonon lines can be observed in highly resolved spectra of electronic excitations of impurities in semiconductors. A theory of this effect in defect semiconductors was proposed by Heine and Henry. Their model is based on the idea that a trapped carrier reduces the force constants between the impurity and its neighbors. This excess carrier density softens the normal-mode frequencies in the lattice, and reduces the zero-point energies of the oscillators. Since the model was proposed for a simple isoelectronic impurity which in the excited state of the optical transition is usually characterized by a free or loosely bound carrier, the mode softening is considered, in this case, only for the ground state when the electron is rather strongly localized around the impurity.

Reasonable agreement with the experimental results was found for various impurities in GaP. One exception, mentioned as not explainable within the scope of their paper, is the isotope shift of the zero-phonon transition producing the so-called a line in ZnO:Cu, which exhibits a negative sign of the effect, contrary to the positive sign predicted by the theory. Photoluminescence excitation spectroscopy (PLE) of the green luminescence band of ZnO:Cu reveals three zero-phonon lines, labeled a, b, and g. So far, no isotope shift for these resonances is resolved in the PLE spectra.

An explanation of the negative isotope shift of the a zero-phonon line (ZPL), proposed by Van Vechten, also includes the excited-state contribution. However, magneto-optical measurements showed that electronic states, playing the leading role in the process, differed from those considered in the model. A phenomenological model for an isotope shift in the spectra of transition-metal impurities was proposed in Refs. 5–7, with the aim of interpreting their experimental data on CdS:Ni. The principal assumption of the model is that different local vibration modes are coupled to the ground and excited states of the transition process. However, a really microscopical approach to the problem of the isotope shift, with a proper account of the electronic structure of transition-metal impurities and its influence on the local vibrational modes, still has to be done.

An interesting isotope shift is observed for the neutral intracenter transition $\text{Cu}^{2+} (2T_2 - 2E)$ (Refs. 7–9) in the same system. The isotope shift for this intracenter transition is found to be negative and to have nearly the same value as for the a transitions. The isotope effect for the intracenter $\text{Cu}^{2+} (2T_2 - 2E)$ transition could not be explained within the Heine and Henry models. Its negative sign as well as the order of magnitude of the isotope shifts for the a line and for the $\text{Cu}^{2+} (2T_2 - 2E)$ transition are still waiting for a proper explanation. Both transitions have the same $\text{Cu}^{2+} (2T_2)$ ground state, but different excited states. It is surprising that these excited states should have the same mass dependence, because their electronic character is different.

In order to complement the available experimental data, we perform high-resolution spectroscopy to measure the $^{63/65}\text{Cu}$ isotope splitting of both transitions at the same crystals. Furthermore, we perform resonant Raman spectroscopy on the $\alpha, \beta$, and $\gamma$ transitions to obtain insight into the local vibrational system of the copper impurity. These experimental results will be the starting point for the complete explanation of both isotope effects within the extended Heine and Henry model.

The mode softening model stresses the sensitivity of the isotope shift to the structure of the electron wave functions. This paper proposes a microscopic approach to the description of the isotope shift for optical transitions in semiconductors doped by transition-metal impurities by taking into account the contribution of the covalent swelling of the electron impurity wave functions into the mode softening effects.
effect. Mode softenings for both the ground and excited states will be of importance. The interplay between them will determine the sign of the isotope shift, which can then easily become negative. This mechanism is applied to the ZnO:Cu system for which experimental data are available. Additional measurements are also carried out. The approach allows us to understand the very close values of the isotope shifts for the $\alpha$ and $\beta$ transitions, and that for the intracenter transition.

**II. EXPERIMENTAL RESULTS**

The samples used for the measurements are high-quality rods of ZnO grown in the laboratories of Professor X. Heiland. The crystals contain copper as an unintentional dopant, and the impurity concentration varies between 10 and 250 ppm. The samples were immersed in liquid helium. Light from the crystal was decomposed by a 0.8-m double monochromator (Spex) and recorded with a Bialkali photomultiplier in the visible or a Ge-detector in the near infrared spectral region. Photoluminescence was excited with the UV lines of an Ar$^+$ or HeCd laser. A dye laser pumped by an excimer laser served as a high-resolution tunable light source for the PLE experiments.

High-resolution spectroscopy in the PLE of the green emission shows an isotope effect for the $\alpha$ as well as $\beta$ zero-phonon lines, while for the $\gamma$ zero-phonon line no isotope shift is observed (see Fig. 1). The $^{63/65}$Cu isotope shift of about 150±10 $\mu$eV is observed for the $\alpha$ and $\beta$ ZPL’s (Fig. 1). The negative sign of the isotope shift indicates that the lighter isotope has a larger ZPL-energy. The FWHM (full width at half maximum) is 60 $\mu$eV for both isotope lines for each transition in high-quality ZnO crystals.

The FWHM for the $\gamma$-ZPL is very large, 670 $\mu$eV, and no isotope shift can be measured. This large FWHM can be explained by the fast nonradiative relaxation within the intermediately bound exciton states. The probability for such nonradiative decay depends on the phonon density of states and the number of phonons needed for the multiphonon relaxation. As the phonon density of states goes to zero with decreasing energies (acoustic branch), the nonradiative transition probability is much larger for the $\gamma$-$\alpha$ transition compared to the $\beta$-$\alpha$ transition, because of the larger energy difference between $\gamma$ and $\alpha$ compared to the $\beta$-$\alpha$ transition.10

For the intracenter Cu$^{2+}$($^2E$) transition two ZPL’s are observed in absorption,8,9 and they are attributed to the $\Gamma_4(2T_2) - \Gamma_5(2E)$ and the $\Gamma_4(2T_2) - \Gamma_5(2E)$ transitions. A highly resolved transmission spectrum of the low-energy ZPL is shown in Fig. 2 (lower part).

The $\Gamma_4(2T_2) - \Gamma_5(2E)$ ZPL also exhibits a negative $^{63/65}$Cu isotope shift of (122±6 $\mu$eV). The value is larger than the previously reported one of (110±30 $\mu$eV), but agrees within the error margin.

In this paper we focus our interest on the comparison between the $^{63/65}$Cu isotope shifts observed for both Cu$^{2+}$($^2T_2$) and [Cu$^{2+}$ - (Cu$^+$,$h$)] transitions. A comparison for both copper isotope shifts in the Cu$^{2+}$ transition and in the $\alpha$ line is shown in Fig. 2. It can be seen that the magnitudes are very close with a small difference of 28 $\mu$eV.

For a detailed understanding of the line structures and the observed isotope shifts, it is important to investigate the local vibrational system of the Cu$^{2+}$($^2T_2$) and Cu$^{2+}$($^2T_2$) transitions. Local vibrational properties of copper in ZnO are investigated by Raman spectroscopy. A Raman spectrum of a copper-doped ZnO crystal (250 ppm) is shown in Fig. 3. For the nonresonant excitation ($E<E_a=2.859$ 86 eV), only the host phonon modes of ZnO are observed. For resonant excitation into the $\gamma$ ZPL of the...
which can be determined independently, the zero-point vibration energies in the electronically ground and excited states,

\[ \delta = \frac{n \hbar}{2} (\Delta \omega_{gs} - \Delta \omega_{ex}) \]

where \( n \) is the degeneracy of the local vibration mode.

\( d \) electrons of the transition-metal impurities may hybridize with the \( p \) states of the valence bands (see, e.g., Refs. 11–15) and form deep levels in the forbidden energy gap of the semiconductor. As a result, the wave function of the trapped electron is a superposition of a strongly localized atomic “core” and an essentially more extended “Bloch tail.” These properties also play an important role in the isotope shift studied in this paper. In particular, the frequency change becomes important not only in the excited state (as it takes place in the simple isoelectronic impurities), but in the ground state as well.

### A. Intracenter transitions

The ninth electron energy of a neutral Cu\(^{2+}\) (\( d^9 \)) impurity in a \(^2T_2\) or \(^2E\) state corresponds to lines lying close to the conduction band, and therefore the corresponding wave functions are hybridized with the conduction-band \( s \) states. The hybridization between the \( d \) and \( s \) states is allowed in hexagonal crystals\(^{16,17}\) when the corresponding matrix element \( V_{\gamma\tau}(\mathbf{k}) \) is not zero at \( \mathbf{k} \rightarrow 0 \).

Therefore, the ninth electron wave functions can be approximately written as a bonding combination of the atomic \( d \)-function \( \psi_{d\Gamma} \) and the Bloch tail \( \varphi_{s\gamma} \),\(^{16,17}\)

\[ \psi_{\gamma\tau} = \frac{1}{\sqrt{1 + M_{\gamma\tau}'}} [\psi_{d\Gamma} + \sqrt{M_{\gamma\tau}'} \varphi_{s\gamma}] \]

where

\[ M_{\gamma\tau}' = - \frac{d M_c(E_{\gamma\tau})}{d E_{\gamma\tau}} \]

and

\[ M_c(\varepsilon) = \sum_k \frac{|V_{\gamma\tau}(\mathbf{k})|^2}{\varepsilon - \varepsilon_c(\mathbf{k})} \]

(c = e) or hole (c = h) wave function. The radii \( R_1 \) and \( R_2 \) in the integral roughly define the corresponding volume.

The local mode frequency is determined by the equation

\[ \omega = \omega_0[1 - \gamma_{p}(c)] \]

where \( \omega_0 \) is the corresponding effective mass. Assuming that the change of the impurity isotope mass by \( \Delta M \) causes the same change of the effective mass, the frequency changes by the value

\[ \Delta \omega = \frac{\Lambda}{2M_0 \omega} \left( \frac{\Delta M}{M} \right) + \gamma_{p}(c) \frac{\Delta M}{M} \]

This sort of a change of the frequency occurs both in the electronically ground and electronically excited states involved in the optical transition. As a result, a change of the ZPL energy occurs and, according to Eq. (1), the isotope shift of the optical line is the difference between the shifts of the zero-point vibration energies in the electronically ground and excited states,
\(E_{\Gamma}\) is the impurity energy level, and \(\Gamma = \frac{\alpha}{2} + \frac{\beta}{2}\).

The isotope shifts for the intracenter transitions, \(\text{Cu}^{2+}(\Gamma_d(2T_2) \rightarrow \Gamma_x(5d^5(E)))\) are calculated using the wave functions \(\psi_{\Gamma_d}\) and \(\psi_{\Gamma_x}\) [Eq. (4)] for the ninth electron of the \(\text{Cu}(d^9)\) in the excited and ground states, respectively. The ground-state wave function transforms according to the irreducible representation \(\Gamma_{ex}=\Gamma_4\), whereas the excited states are degenerate and transform as \(\Gamma_{ex}=\Gamma_5\) and \(\Gamma_6\).

The mode softening is caused by the Bloch tail parts \(\phi_{\Gamma}\) of the impurity wave functions (4). Rough estimates can be done using the approximate expression (see, e.g., Chap. 7 in Ref. 15)

\[
\varphi_\Gamma = A^{-1/2} e^{-k_{\Gamma R}/k_{\Gamma R}},
\]

where \(k_{\Gamma R} = (2m^* \Delta_\Gamma / h^2)\) and \(\Delta_\Gamma = E_{\Gamma} - E_{0\text{e}}\), and \(E_{0\text{e}}\) is the bottom of the conduction band.

Then, using Eq. (3), the isotope shift for the intracenter transition reads

\[
\delta = \frac{n}{4} \hbar \omega \frac{M}{M} \gamma_\Gamma \Delta P_{\text{intra}}.
\]

Equation (6) yields the probability of finding the impurity d electron in the first coordination sphere

\[
P_{\Gamma} = \frac{M'_{\Gamma}}{1 + M'_{\Gamma}'} \left( e^{-2k_{\Gamma R}R_1} - e^{-2k_{\Gamma R}R_2} \right),
\]

and its change in the course of the intracenter transition is

\[
\Delta P_{\text{intra}} = P_{\text{exc}} - P_{\text{g}} = 0.221 \frac{M'_{\Gamma}}{1 + M'_{\Gamma}'} - 0.327 \frac{M'_{2T_2}}{1 + M'_{2T_2}}.
\]

The following values of the parameters are used: \(m^* \approx 0.4 m_0\), \(\Delta_\Gamma \approx 0.94\) eV (ground state), \(\Delta_\Gamma \approx 0.2\) eV (excited states), \(R_1 = 0.64\) Å, and \(R_2 = 1.7\) Å.

\[\text{B. Bound excitons}\]

Transitions

\[\text{Cu}^{2+}(2T_2) \rightarrow [\text{Cu}^{+}(d^9 + e), \hbar]\]

in \(\text{ZnO}:\text{Cu}\), creating an exciton bound to the impurity, are now considered. There are three corresponding spectral lines called \(\alpha, \beta,\) and \(\gamma\) lines, and for the first two of these an isotope shift is measured.

The exciton wave function \(\Psi_{\text{exc}}(d^{10}, \hbar)\) is a product of the wave functions of the tenth d electron of the Cu impurity and that of the loosely bound hole. The tenth electron wave function in \(\text{ZnO}:\text{Cu}\) \(\psi_{\text{d}^{10}}\) can be represented as a bonding combination of type (4), with the only difference that the electron energy \(E_{\Gamma}\) is now that of the tenth (0.19 eV) electron in the ground state, rather than 0.94 eV of the ninth.

The hole wave function \(\psi_{\text{h}}, (n=1, 2, \ldots, 10)\) is formed by the normalized pseudo-wave-function \(\psi_{\text{h}}\) and the core part \(\psi_{\text{d}^{10}}(\text{Cu})\) of the Cu(\(d^{10}\)) states, where

\[
F_d = \frac{\left( \gamma_{\text{h}} | W | \psi_{\text{h}} \right)}{E_{\gamma} + E_{\text{h}}},
\]

Now the isotope shift for the \(\alpha\) and \(\beta\) transitions in \(\text{ZnO}:\text{Cu}\) is calculated. The ground state for both these transitions coincide with that of the intracenter transition discussed in Sec. III A. Therefore, the corresponding contribution to the isotope shift is just the second term on the right-hand side of Eq. (8). An exciton is bound to the impurity in the excited state, which causes the change of the electron density in the first coordination sphere. The exciton electron increases the density, whereas the hole decreases it. The resulting contribution to the isotope shift reads

\[
\gamma_{\text{e}} P_{\text{exc}} = \gamma_{\text{e}} \left[ P_{\gamma}(\alpha) - P_{\beta}(\beta) \right],
\]

where the electron value \(\gamma_{\text{e}}\) of this material constant is chosen, since the electron contribution to the density in the first coordination sphere is larger than that of the hole.

Using Eq. (4) (with the changed energy) for the electron wave function, and Eq. (9) for the hole wave function, one arrives at

\[
P_{\text{exc}} = 0.216 \frac{M'_{2T_2}(d^{10})}{1 + M'_{2T_2}} - P_{\beta}(\beta).
\]

Here the electron ionization energy \(E_{\gamma}(0/-) \approx 3.25\) eV (Refs. 19 and 20) is used, meaning that \(\Delta_\Gamma = 0.19\) eV.

The hole contribution

\[
P_{\beta}(\beta) = 0.1658
\]

in Eq. (10) is found using the value \(m^* = 1.8 m_0\) (Ref. 8) of the hole effective mass. The experimental value \(\Delta_{\text{hole}} \approx 0.4\) eV (Refs. 19 and 20) of the hole binding energy results in the hybridization parameter \(F_{\text{d}}/|1| \approx 0.2\), which is quite reasonable for this level.

The large value \(M'_{2T_2} \approx 1\) (see, e.g., Refs. 16 and 17) for the electron energy lying close to the bottom of the conduction band means that the excess electron density is really larger than that of the hole, as was assumed above. Therefore, one obtains the change \(P_{\text{exc}} = 0.0368\) of the carrier density in the first coordination sphere, due to the bound exciton, and finally arrives at the change

\[
\Delta P_{\text{exc}} = 0.0368 - 0.327 \frac{M'_{2T_2}}{1 + M'_{2T_2}}
\]

of the excess electron density in the course of the \(\alpha\) and \(\beta\) transitions.

\[\text{C. Comparison of the results for the intracenter transition and the bound exciton excitations}\]

It was experimentally found that the isotope shifts in the two above cases, the intracenter transition and excitation of a bound exciton, are rather close to each other (see Sec. II). The same value of \(\Delta P_{\text{intra}}\) [Eq. (8)] is obtained for the hy-
bridization parameter $M'_{cE}=0.2$, which is a reasonably small value for the $\Gamma_{x,y}(2E)$ state whose hybridization with the conduction-band states is symmetry forbidden. Hence Eq. (8) becomes

$$\Delta P_{\text{intra}} = \left( 0.0368 - 0.327 \frac{M'_{c2T_2}}{1 + M'_{c2T_2}} \right) \gamma_e.$$  \hspace{1cm} (12)

Using the above value of the parameter $M'_{c2E}$, Eqs. (11) and (12) produce negative and equal values of the electron density differences $\Delta P_{\text{ex}}$ and $\Delta P_{\text{intra}}$. The correct value of the isotope shift $\delta$ [Eq. (3)] is obtained by using the coefficient $\gamma_e = 2.7$ measured in Ref. 4.

The local phonon mode $T_2$, in which the Cu atom takes part, is assumed to be responsible for the electron-phonon interaction. Due to the $C_{3v}$ symmetry of the center, this vibration mode splits into $A_1$ and $E$ modes. Resonance Raman measurements of the $\text{Cu}^{2+}(\beta T_2)-(\text{Cu}^{1+}, h)$ transition (Fig. 3) show that two additional modes at 49.47 and 68.83 meV with the symmetry $E$ and $A_1$, respectively, appear.

We assume that the $A_1$ mode with the energy $h\omega = 68.83$ meV and degeneracy $n = 1$ plays the leading role in ZnO:Cu (see also Refs. 21 and 22). Using the mass ratio $\Delta M/M = 2/63$ for the $\text{Cu}^{36}6\text{Cu}$ isotope exchange, the observed isotope shift $\delta = -0.14$ meV is obtained by choosing the hybridization parameter $M'_{c2T_2} = 0.66$, meaning that 40% of the electron wave function is outside the core. The estimate that 40% of the $2T_2$ electron wave function in Cu$^{2+}$ is an explanation for the large $g$ shift for Cu$^{2+}$ in ZnO, as concluded in Ref. 8. The hybridization of the $2T_2$ level is expected to be larger than that of the $2E$ state, due to the wurtzite symmetry of this crystal, in which a hybridization of the $2T_2$ with the conduction band states is allowed.\textsuperscript{16,17}

### IV. SUMMARY

A mechanism is proposed, according to which the covalent swelling of the electron wave functions in transition-metal impurities, combined with the mode softening mechanism, makes it possible to understand the sign and value of the isotope shift for various optical lines. A $d$-electron wave function consists of a $d$-type “core” and a “Bloch tail” constructed from the band states. The latter is responsible for the mode softening, which gives rise to a sensitivity of the isotope shift to the hybridization properties both in neutral and charged impurity states.

Contrary to mode softening in simple impurities, which takes place only in the ground state of the system, mode softening in both ground and excited states of transition-metal impurities must be properly accounted for. The effect depends strongly on the covalency factor $M'_{\text{af}}$, whose value is a function of the position of the $d$ levels in the energy gap and of the symmetry of the system.

This model is applied for an interpretation of the experimental data reported here for ZnO:Cu. These data give better-resolved $\alpha$-line PLE spectra. The isotope shift for the $\beta$ line and its absence for the $\gamma$ line is reported for the first time, to our knowledge.

Our model allows one to understand the isotope shift for both intracenter and charge-transfer transitions in transition-metal impurities. By using the proper wave functions of the neutral Cu$^{2+}(d^9)$ ion and the [Cu$^{1+}(d^9 + e), h]$ excited state, close values and signs of the isotope shifts for both the intracenter transition and for $\alpha$ and $\beta$ ZPL’s are explained.

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