



Local vibrational modes of the CuO_4 -cluster in ZnO

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Abstract

Zero phonon line isotope shifts of d–d transitions depend on the local vibrational properties of the transition metal. For copper in ZnO this isotope effect depends not only on the mass of the copper impurity but also on the mass of the oxygen ligands. To explain this behavior the local vibrational properties of copper in ZnO are investigated by means of resonant Raman spectroscopy and analyzed in a cluster calculation in the valence force model of Kane using the scaling factor approximation. The fit of the experimental data together with the calculations give insight into the local binding properties around the impurity, the localization and the symmetry of the local vibrational modes. The copper incorporation results in a local bond softening in the ZnO lattice. The copper and the oxygen mass dependences of the local vibrational modes of the CuO_4 -cluster are calculated. The mass dependence is mainly determined by the localization of the local vibrational modes. The anisotropic vibration of the CuO_4 -tetrahedron explains the ligand induced zero phonon line isotope shift which was observed for the intracenter $\text{Cu}^{2+}({}^2\text{T}_2-{}^2\text{E})$ transition.

1. Introduction

Copper is a luminescence activator in II–VI compounds and gives rise to various luminescence and absorption bands [1–3]. In ZnS, CdS and ZnO there are two transitions with Cu^{2+} as a ground state. One is the intracenter $\text{Cu}^{2+}({}^2\text{T}_2-{}^2\text{E})$ transition and the other is the $\text{Cu}^{2+}-(\text{Cu}^+, \text{h})$ charge transfer transition. Despite these similarities, there are some striking differences for copper in the sulfide compounds and in ZnO.

Compared to ZnS and CdS, the Cu^{2+} acceptor is deeper in ZnO. The binding energies are 1.293, 1.20 and 3.25 eV, respectively [3,4]. As a consequence the relaxation behavior of the excited (Cu^+, h) states is totally different. The decay of these states in ZnS

and CdS is totally nonradiative, whereas in ZnO a complete radiative decay occurs [5]. On the other hand the $\text{Cu}^{2+}({}^2\text{E}-{}^2\text{T}_2)$ transition has a higher luminescence efficiency in ZnS and CdS than in ZnO. The nonradiative relaxation rate is determined mainly by multiphonon transition and is thus directly connected with the local vibrational properties of the center [6]. Another striking feature of copper in ZnO is the negative ${}^{63/65}\text{Cu}$ isotope splitting of the $\text{Cu}^{2+}({}^2\text{E}-{}^2\text{T}_2)$ and the $(\text{Cu}^+, \text{h})-(\text{Cu}^{2+}({}^2\text{T}_2))$ zero phonon lines (ZPLs) which is not observed for the corresponding transitions in ZnS and CdS [3,4]. The negative isotope shift is unique amongst all intracenter transitions known for 3d elements in II–VI compounds. Recently, a ligand induced isotope shift was observed for ZnO:Fe,Ni,Cu [7]. Isotope shifts of ZPLs are analyzed in the framework of local vibrational properties of the center [8].

The aim of this paper is to give a detailed study on local vibrational modes (LVMs) of Cu in ZnO by

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means of resonant Raman spectroscopy and to describe cluster calculations to elucidate the above mentioned peculiarities of the copper center.

2. Experimental results

A transmission spectrum of the $\text{Cu}^{2+}(\Gamma_4(^2T_2)-\Gamma_{5,6}(^2E))$ -ZPL is shown in Fig. 1. The two ZPLs (a) correspond to the Cu^{2+} transition for ^{63}Cu and ^{65}Cu . These ZPLs exhibit a negative $^{63/65}\text{Cu}$ isotope shift of $-61 \pm 3 \mu\text{eV}$ per nucleon. Additional to the 2 main ZPLs for $^{63/65}\text{Cu}$ four weak satellites on the low energy side occur. The shift and the intensity ratio (in brackets) of the satellite lines (b) and (c) with respect to the ZPLs (a) are $-180 \mu\text{eV}(0.61 \pm 0.05\%)$ and $-205 \mu\text{eV}(0.20 \pm 0.05\%)$. These ZPLs are attributed to isotope shifts within the five-atom CuO_4 -cluster, where one of the four ^{16}O -ligands is replaced by an ^{18}O -atom. Due to the fact that the CuO_4 -cluster is slightly distorted in the direction of the c -axis only three off-axis oxygen places remain equivalent. This explains the intensity ratio of 3 : 1 between the lines (b) and (c). The observed intensity ratio between the ZPLs (a), (b), and (c) corresponds to the natural isotopic abundancies for the three different CuO_4 -clusters which were 99.051, 0.596

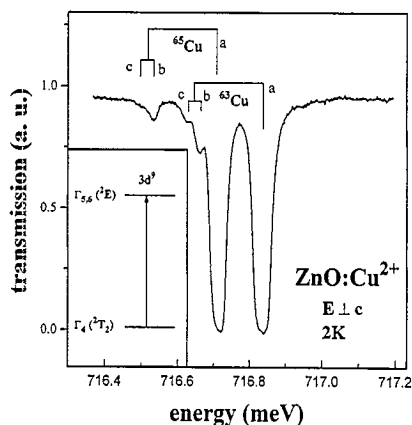


Fig. 1. Linear transmission spectrum of the $(\Gamma_4(^2T_2)-\Gamma_{5,6}(^2E))$ transition of the Cu^{2+} -center in ZnO. Additional to the $^{63/65}\text{Cu}$ -isotope ZPLs (a) two satellite lines (b,c) are observed. These satellite lines are attributed to recombination within the CuO_4 -cluster, where one of the ^{16}O -ligands is substituted by an ^{18}O -atom. For the case (b) the off-axis ^{16}O is substituted, for the case (c) the c -axis oxygen is replaced.

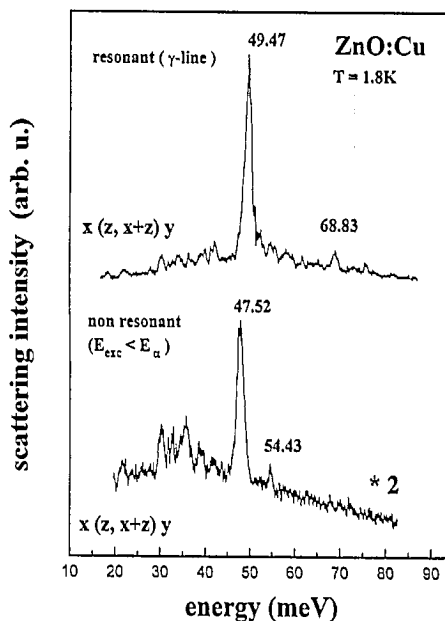


Fig. 2. Raman spectra of ZnO:Cu^{2+} under non-resonant excitation (lower half) and resonant excitation of the $\text{Cu}^{2+}-(\text{Cu}^+,h)$ charge transfer transition (upper half). The LVMs of the copper center are only observed under resonant excitation and the energy is indicated.

and 0.199%. The oxygen-isotope splitting is also negative but the order of magnitude is larger than the $^{63/65}\text{Cu}$ -splitting. Similar ligand induced isotope shifts are also observed for ZnO:Fe^{3+} and ZnO:Ni^{3+} [7].

To get insight into the local vibrational properties of the center, resonant Raman spectroscopy on the $\text{Cu}^{2+}(^2T_2)-(\text{Cu}^+,h)$ transition was performed (Fig. 2). For non-resonant excitation ($E < E_\alpha = 2.858858 \text{ eV}$) only the two main host phonon modes are observed. For resonant excitation into the γ -ZPL of the $\text{Cu}^{2+}(\Gamma_4(^2T_2))-(\text{Cu}^+,h)$ transition at 2.87284 eV, two additional modes at 49.47 meV and 68.83 meV appear. These modes are attributed to LVMs of the copper center.

3. Fit of the LVMs in the Kane model and discussion

In order to elucidate these results, calculations of the local vibrational properties of the CuO_4 -cluster in ZnO are performed. Since we are interested in the

calculation of local vibrations, the most important feature is the change of valence force parameters in the vicinity of the defect. Therefore, a valence force model can be used if it correctly describes the optical and high energy acoustical phonon branches of the dispersion curve. This can be already achieved with the valence force model of Kane [9]. Here, the nearest neighbor bond stretching and bond bending forces interactions with farther distant atoms as well as the Coulomb interaction are also included. The cluster contains 77 atoms arranged in 17 shells. The first shell is the central Zn-atom of the cluster. The remaining shells are ordered by the distance of the shell atoms to the central atom, i.e. the second shell is given by the ligand atom in the *c*-axis direction and the third shell represents the three ligands in the off-axis position. First, the dispersion curve as well as the phonon density of states are fitted giving the parameters of the ideal crystal. We achieve an almost perfect agreement for the host modes above 22.3 meV with a maximum error of 0.5 meV. For the TO(Γ) phonon at 12.5 meV we obtain the largest deviation of 0.8 meV, which is due to the finite cluster size. The local vibrational properties are calculated taking the Cu-atom as the central atom of the cluster. In our calculation a phonon mode is called local if the localization within the first three shells is more than 50%. Now the dependence of the symmetry, the energy and the localization of the modes on the scaling factor is determined. The scaling factor s is a measure of the change of the interatomic force constant near the disturbing center. In the scaling factor approximation all impurity related parameters are changed in the same way. This means if p is the parameter of the ideal crystal the impurity parameter p_{TM} is given by $p_{TM} = p + sp$.

The energy of the LVMs of the Cu-center as function of the scaling factor are shown in Fig. 3. We obtain 4 LVMs with A_1 and E symmetry, listed in Table 1. We achieve the best agreement with the two observed modes for a negative scaling factor of -0.35 . This indicates a local bond softening in the ZnO lattice due to the copper incorporation. The lattice softening caused by the copper incorporation is also known from the high T_c superconductors. This behavior is also unique amongst other 3d elements in ZnO. For Fe, V, and Ni we obtain positive scaling factors of about 0.6, 0.7 and 0.5. Further-

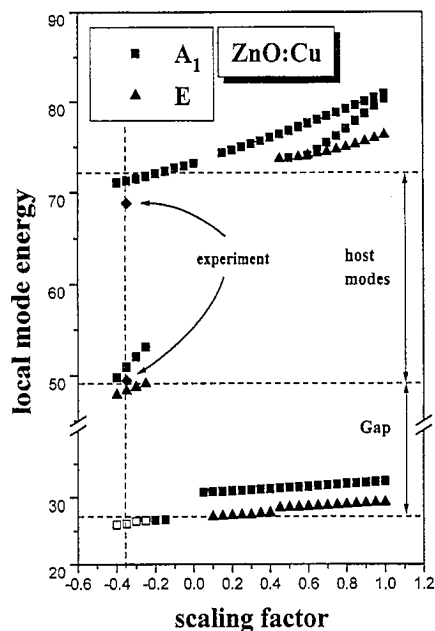


Fig. 3. Energy of the LVMs in dependence on the scaling factor for ZnO:Cu. For $s = -0.35$ an agreement with the experimental data is obtained. The energy of the host phonon modes is indicated by the dashed lines.

more, positive scaling factors of 0.2 and 0.1 are also obtained for ZnS:Cu and CdS:Cu. This demonstrates the strange role of copper in an oxygen environment. In order to calculate the mass dependence $\partial E / \partial M_{Cu}$ of the LVMs the Cu-atom ($M_{Cu} = 63.54$) is replaced by the isotopes ^{63}Cu and ^{65}Cu . The largest relative mass dependence is observed for the A_1 -mode at 26.08 meV (Table 1). The mass dependence is directly connected with the localization of the local phonon modes. With increasing localization at the Cu-center the mass dependence increases.

Table 1
Energy, symmetry and mass dependencies $\partial E / \partial M$ of the LVMs of the CuO_4 -cluster in ZnO

E_{exp} (meV)	E_{calc} (meV)	Symmetry	$\partial E / \partial M_{Cu}$ (meV/nuc)	$\partial E / \partial M_O$ (b) (meV/nuc)	$\partial E / \partial M_O$ (c) (meV/nuc)
68.83	71.25	A_1	-0.0001	-0.0019	-0.2968
-	50.91	A_1	-0.0147	-0.0169	-1.2178
49.47	48.31	E	-0.0004	-0.5136	-0.0618
-	26.36	A_1	-0.0210	-0.0012	-0.4855

The energy values of the LVMs are given for natural abundance values of the copper and oxygen mass. For the case b (c) one of the off-axis (*c*-axis) oxygen atoms is substituted.

To explain the two types of the observed ligand induced isotope shift (Fig. 1), calculations of the local vibrational properties of the CuO_4 -tetrahedron in the 77 atomic cluster are also performed. Here, the dependence of the energy of the 4 LVMs on the oxygen mass is determined. Thereby, the Cu-mass is fixed at $M_{\text{Cu}} = 63.54$ and one of the four ^{16}O -ligands is replaced by ^{17}O and ^{18}O . For the case (b) one of the off-axis ligands is replaced and for the case (c) the c -axis oxygen is substituted. The results are summarized in Table 1. Several LVMs depend apparently on the oxygen mass. It is a striking fact that the three low energy LVMs exhibit a totally different behavior in their mass dependencies $\partial E/\partial M_{\text{O}}$ for the cases (b) and (c). The A_1 -modes are mainly influenced by the replacement of the c -axis oxygen, whereas the E-mode is effected by the replacement of the off-axis oxygen. This is due to the anisotropical oxygen vibration within the CuO_4 -cluster. If we remove the trigonal distortion in the calculation the anisotropy vanishes. As a consequence of the anisotropy the localization and the mass dependences of the LVMs are different. For the low energy A_1 -mode in case (c), hybridization with the host phonon modes for increasing oxygen mass occurs, whereas for the A_1 - and E-modes at 50.91 and 48.3 meV the hybridization becomes weaker with increasing oxygen mass.

However, to explain the ZPL isotope shifts quantitatively, the Jahn–Teller effect has to be taken into account. For Cu^{2+} , both the excited 2E and the 2T_2 -ground state are Jahn–Teller active. It is expected that the Jahn–Teller effect is stronger in the

2T_2 -ground state than in the excited 2E and (Cu^+,h) states. Due to the fact that the isotope shift is negative for both transitions, the mass dependence of the excited states is stronger than the ground state mass dependence. This is in agreement with the statement that the Jahn–Teller effect reduces the mass dependence of a state [8]. If we assume that the differences of the isotope mass in the CuO_4 -cluster is negligible for the Jahn–Teller coupling then the order of magnitude of the isotope effects is determined only by the mass dependences of the LVMs. The results of our calculation support this assumption, because the copper mass dependence of the LVM at 26.0 meV is smaller than the oxygen mass dependencies of the LVMs at 48.3 and 71.2 meV.

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