

LIGAND INDUCED ISOTOPE SHIFTS OF TRANSITION METAL CENTERS IN ZnO

P. Thurian, R. Heitz, S. Kleinwächter, A. Hoffmann, and I. Broser
Institut für Festkörperphysik, Hardenbergstr. 36, 10623 Berlin, Germany

ABSTRACT

High resolution spectroscopy of transition-metal (TM) doped ZnO leads to the detection of new zero phonon lines in the spectra of the d-d transitions of Cu^{2+} , Ni^{3+} and Fe^{3+} . On the basis of statistical considerations these lines are attributed to ligand induced isotope shifts. The distribution of different O-isotopes in the (TM- O_4)-cluster leads to separated lines in the d-d spectra of the TM. These ligand induced isotope shifts are discussed in a general model, cited in [1], giving new insight into the local vibrational system of the TM-centers and the electron-phonon interaction.

1) INTRODUCTION

The incorporation of different transition metal (TM) isotopes leads sometimes to the detection of zero phonon line (ZPL) shifts for the d-d transition, depending on the isotope mass. Prominent examples are the isotope shifts of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ [2], $\text{CdS}:\text{Ni}^{2+}$ [1,3], $\text{ZnO}:\text{Cu}^{2+}$ [4], $\text{ZnO}:\text{Ni}^{3+}$ [5] and $\text{ZnO}:\text{Fe}^{3+}$ [6]. These shifts are in the order of some 10 μeV /nucleon and analyzed in the framework of local vibrational properties of the center [1,2,7]. Recently, a ligand induced isotope effect has been observed for the first time on Fe doped ZnO [6] and interpreted with the cooperation of mass dependent local modes, the Jahn-Teller interaction and the C_{3v} -crystal field. The aim of this contribution is to present a comprehensive description of this new kind of phenomena on the basis of additional experimental data.

2) THE ISOTOPE SHIFT-THEORETICAL REMARKS

Isotope shifts observed for optical transitions can be understood on the basis of different mass dependencies of the total energies E of the impurity system in the ground and excited electronic states.

$$\left(\frac{dE}{dM}\right)_{\text{transition}} = \left(\frac{dE}{dM}\right)_{\text{excit}} - \left(\frac{dE}{dM}\right)_{\text{ground}} \quad (1)$$

A general model to describe isotope shifts of TM-ions was elaborated by Hoffmann and Scherz [1]. They assume, that the energy E of an electronic state depends on the spin-orbit coupling (ξ), the Jahn-Teller energy E_{JT} , the orbital-reduction factor k , and the energy $\hbar\omega_i$ of the local phonon mode. This means, that E is given by $E = E(\xi, E_{JT}, k, \hbar\omega_i)$. In first order only the local phonon energy depends on the impurity mass. Thus, the mass dependence dE/dM of each state is given by the formula:

$$\frac{dE}{dM} = \sum_i \frac{\partial E}{\partial \hbar\omega_i} \frac{\partial \hbar\omega_i}{\partial M} \quad (2)$$

Therefore, the mass dependence of each state can be split in a sum of products. Each product contains the mass dependence $\partial \hbar\omega_i / \partial M$ of the phonon modes $\hbar\omega_i$, and the dependencies $\partial E / \partial \hbar\omega_i$ of the total energy of the impurity system in a given electronic state. In terms of the equations 1 and 2 isotope shifts are observed if one of the two product terms in the mass dependence dE/dM of each state is different. An isotope shift is called positive (negative), if the ZPL of the heavier (lighter) isotope is shifted towards higher energy. In general a stronger (weaker) mass dependence of the excited state compared to the ground state results in a negative (positive) isotope shift. It is evident, that observed isotope shifts give new insights into the fine-structure, the local phonon spectrum and the electron-phonon interaction of the TM-impurity in the host crystal.

3) EXPERIMENTAL SETUP

The investigated samples are high-quality rods of ZnO grown in the laboratories of Professor Heiland and Professor Mollwo. The crystals have dimensions in the mm range and contain Cu, Fe and V as unintentional dopants. The Ni doping was performed afterwards by indiffusion of natural $^{58/60}\text{Ni}$ and enriched ^{62}Ni and ^{64}Ni isotopes. In general, the 3d impurity content is in the sub ppm to ppm range. The crystals are immersed in liquid He at temperatures of about 2K. The PL is excited by the blue lines of a 5W Ar⁺ ion laser or the UV lines of a He-Cd laser. For the absorption experiments a tungsten-halogen lamp is used. The light is decomposed in a 0.75m double grating spectrometer and recorded with a cooled GaAs multiplier or a germanium detector.

4) EXPERIMENTAL RESULTS

In this contribution ZPL isotope shifts for the d-d transitions of Cu^{2+} , Ni^{3+} and Fe^{3+} centers substituting the cation in the ZnO host crystal are investigated. The TM-induced as well as the ligand induced isotope shifts are closely related to the well-known fine-structure of each transition which is briefly summarized in the following.

4.1) TRANSITION METAL INDUCED ISOTOPE SHIFTS

The fine-structure of each transition is influenced by spin-orbit coupling, trigonal crystal field and a Jahn-Teller effect.

Cu^{2+} (3d⁹-system) gives rise to an intense infrared 2T_2 - 2E absorption band in the 0.72eV spectral region [4]. The corresponding emission is extraordinary weak and could be detected recently [8,9]. The $(\Gamma_4({}^2T_2))$ - $(\Gamma_{5,6}({}^2E))$ -ZPL exhibits a negative $^{63/65}\text{Cu}$ isotope shift of $-61 \pm 3 \mu\text{eV}$ per nucleon (Fig. 1). The value is larger than the reported one of $-55 \pm 15 \mu\text{eV/nucleon}$ [4], but agrees within the margin of error.

Fe^{3+} (3d⁵-system) reveals a visible 4T_1 - 6A_1 emission in the 1.78eV spectral region [6]. The $(\Gamma_4({}^4T_1))$ - $(\Gamma_4({}^6A_1))$ -ZPL shows a positive $^{54/56}\text{Fe}$ isotope shift of $39 \pm 3 \mu\text{eV}$ per nucleon [6].

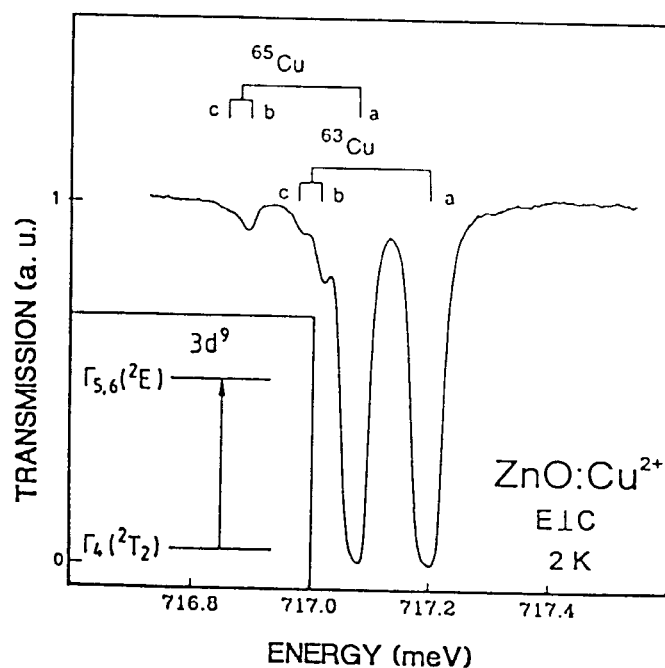


Fig. 1: Linear transmission spectrum of the $(\Gamma_4({}^2T_2))$ - $(\Gamma_{5,6}({}^2E))$ -transition of the Cu^{2+} -center (3d⁹-system) in ZnO at 2K. Additional to the main $^{63/65}\text{Cu}$ -isotope-ZPLs (a) two satellite lines (b, c) are observed. These satellite lines are attributed to recombination within the fiveatomic TM- 16O_4 cluster, where one of the ^{16}O -ligands is substituted by an ^{18}O -atom.

Ni^{3+} (3d⁷-system) leads to an intense near infrared 4T_1 - 4A_2 emission band in the 0.77eV spectral region. The $(\Gamma_{5,6}({}^4T_2))$ - $(\Gamma_{5,6}({}^4A_2))$ as well as the $(\Gamma_{5,6}({}^4T_2))$ - $(\Gamma_4({}^4A_2))$ -ZPLs show positive Ni isotope shifts of $13.5 \pm 1 \mu\text{eV}$ per nucleon [5].

It should be mentioned that for Fe^{3+} and Ni^{3+} only the excited 4T_1 and 4T_2 -states are Jahn-Teller active in first order, whereas for Cu^{2+} both 2T_2 and 2E states are Jahn-Teller active. For $\text{ZnO}:\text{Fe}^{3+}$ only a coupling with E-modes is assumed [6], whereas for $\text{ZnO}:\text{Cu}^{2+}$ a dominant T_2 -mode coupling is probable [7]. The C_{3v} splitting of the T_2 -phonon modes in ZnO are small compared to the Jahn-Teller, the spin-orbit and the phonon energy. Thus, for Jahn-Teller considerations the C_{3v} -field can be neglected. However, it causes a mixing between E and the former T_2 -modes and explains the TM-isotope shift of $\text{ZnO}:\text{Fe}^{3+}$.

4.2) LIGAND INDUCED ISOTOPE SHIFTS

It is a striking fact that for each transition additional weak satellites occur. For Cu^{2+} and Fe^{3+} two

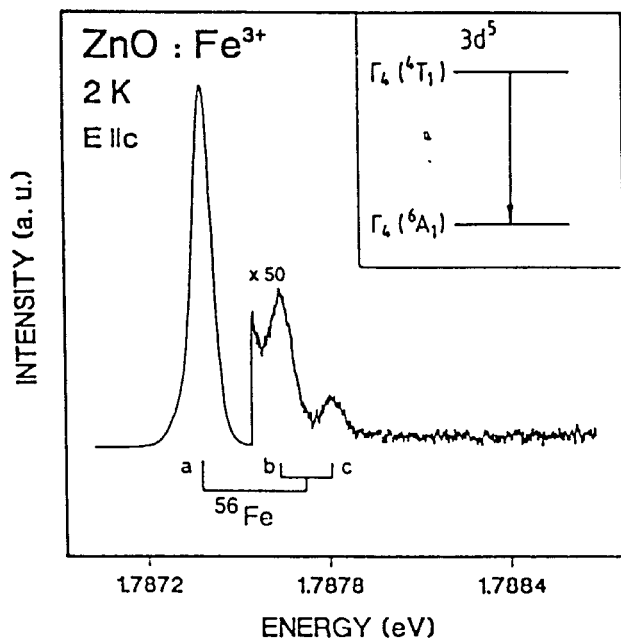


Fig. 2: Emission spectrum of the ($\Gamma_4(4T_1)$ - $\Gamma_4(6A_1)$)-transition of the Fe^{3+} -center ($3d^5$ -system) in ZnO at 2K. The crystal is excited with the 458nm line of an Ar⁺-ion laser. Additional to the main ZPL (a) two satellite lines (b, c) are observed, which are attributed to ligand induced isotope shifts.

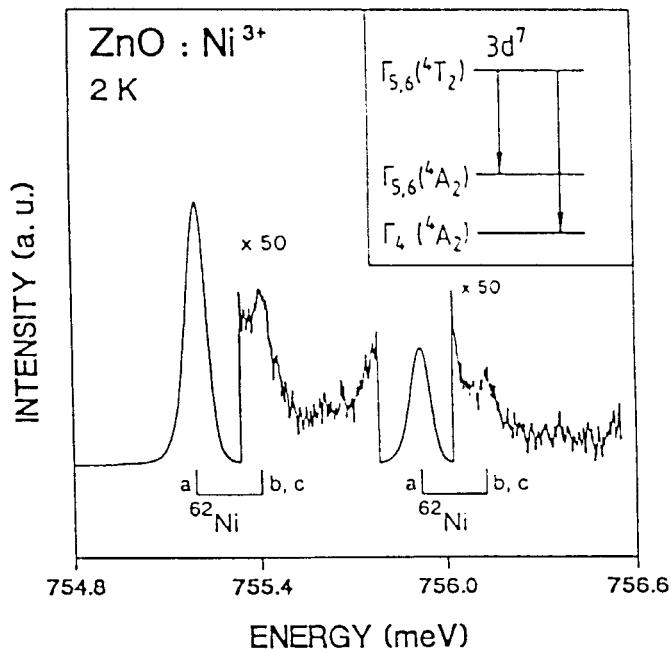


Fig. 3: Emission spectrum of the ($\Gamma_{5,6}(4T_2)$ - $\Gamma_{5,6}(4A_2)$) and the ($\Gamma_{5,6}(4T_2)$ - $\Gamma_4(4A_2)$)-transitions of the Ni^{3+} -center ($3d^7$ -system) in ZnO:⁶²Ni at 2K. The crystal is excited with the 325nm line of an He-Cd-ion laser. Additional to the main ZPLs of each transition (a) one satellite line is observed, which is attributed to a ligand induced isotope shift.

satellite lines, called b and c, are observed for each TM isotope ZPL (Fig. 1, 2). The shift and the intensity ratio of the satellite lines b and c with respect to the main ZPLs (a) are $-180\mu\text{eV}$ ($0.60 \pm 0.05\%$) and $-205\mu\text{eV}$ ($0.20 \pm 0.05\%$) for copper and $222\mu\text{eV}$ ($0.63 \pm 0.05\%$) and $365\mu\text{eV}$ ($0.18 \pm 0.05\%$) for iron. Only one satellite line is detected for the Ni^{3+} -transition. Here, a shift of $208\mu\text{eV}$ and an intensity of ($0.80 \pm 0.05\%$) with respect to the strong ^{62}Ni ZPLs (a) is observed (Fig. 3). The observed shifts as well as the intensity ratio of all satellite lines are summarized in fig. 4. It should be mentioned that these additional lines show the same polarization behavior as the main ZPLs. The intensity ratio does not depend on the investigated crystal or on the crystal temperature. The Zeeman-behavior is the same, too, and the overall behavior indicates further TM centers from these ZPLs, which are just slightly shifted in energy. Due to the fact, that the hexagonal phase of ZnO is very stable, no polytypes, as in the case of ZnS [10, 11], are reported and could therefore be excluded in our interpretation. Furthermore, differently doped and tempered crystals exhibit the same intensity ratio between the main and the satellite ZPLs, which excludes structural imperfections of the crystals or possible TM-associates. The overall experimental features indicate an isotope splitting. Possible remaining isotopes are the oxygen ligands of the TM-ion. Oxygen has three stable isotopes ^{16}O (99.762%), ^{17}O (0.038%) and ^{18}O (0.200%). From a simple statistical consideration it follows, that the possibility to find only ^{16}O ligands in the (TM- O_4)-cluster is 99.051% and the finding of one ^{18}O -atom in the cluster is 0.795%. In hexagonal ZnO the (TM- O_4)-cluster is slightly distorted in the direction of the c-axis and only three of the off-axis oxygen places remain equivalent. The probability to find the ^{18}O ion in the direction of the c-axis is 0.199% and the off-axis place has a probability of 0.596%. The contribution of the ^{17}O -atom is 0.038%, but it can be neglected due to the signal to noise ratio in the observed spectra. It should be pointed

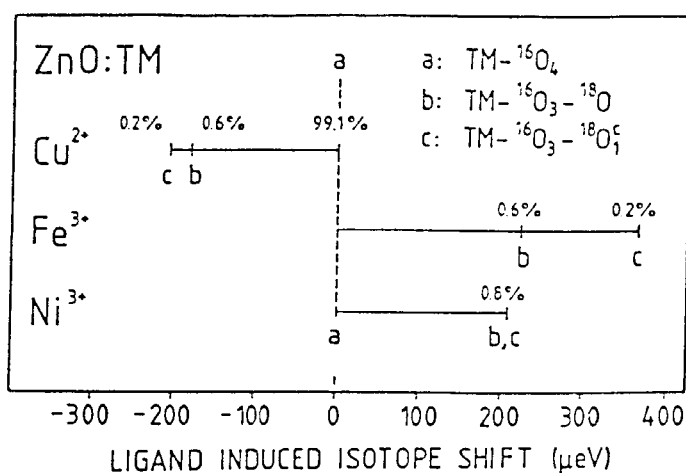


Fig. 4: Observed ligand induced isotope shifts for ZnO:Cu²⁺, Fe³⁺ and Ni³⁺. The energy shift is given with respect to the main TM-¹⁶O₄-ZPL (a). Due to the distortion of the TM-O₄-tetrahedron in the direction of the c-axis, two different ¹⁸O-ligand induced isotope shifts are observable, depending on the position of the substituted ¹⁶O-ligand. The observed relative intensity ratio of the different ZPLs is also indicated.

In general, it is expected that $\partial\hbar\omega_i/\partial M$ is negative, i. e. the phonon energy decreases with increasing isotope mass. A measure for the derivation $\partial\hbar\omega_i/\partial M$ is the contribution of the motion of the impurity ion to the energy of the local mode. In particular, considering local impurity modes mainly localized in a tetrahedrally coordinated five atomic (TM-O₄)-cluster. Here, the T₂-modes which move the central atom influence the TM-isotope shift, whereas a ligand induced isotope shift is caused by the modes which move the ligands strongest. In ZnO the low energy modes peaking at 11.9meV, 16.0meV and 29.0meV mainly move the TM-atom, whereas the high energy optical modes above 46.9meV mainly move the ligands [12]. In the systems investigated in this contribution, only for Cu²⁺ the emission [9] and absorption sideband [4] can be detected up to now. The local optical phonon-modes in the 50-70meV region are only observed in the vibronic spectrum of the excited ²E-state. For Ni³⁺ and Fe³⁺ these high energy modes appear in the sideband of the ⁴A₂ and ⁶A₁ ground states, respectively. Thus it can be summarized, that the local optical modes in the 50-70meV region are observed in the vibronic spectra of the slighter Jahn-Teller active states. They give rise to a strong vibration of the oxygen ligands [12] and cause mainly the ligand induced isotope shifts. The dependence $\partial E/\partial\hbar\omega_i$ of the total energy of an impurity center on the phonon-energy is larger than zero. If the phonon mode of interest is not subject of an electron-phonon coupling then it contributes $(n + g/2)\hbar\omega_i$ to the total energy E and $\partial E/\partial\hbar\omega_i$ becomes $(n + g/2)$ where g is the degeneracy of the phonon mode ($g=3$ for a T₂-mode). These non Jahn-Teller active modes should contribute in the sideband of both ground and excited states, but in terms of eq. 2 they do not influence the observed isotope shift. This is altered if the phonon mode couples to the electronic state via the Jahn-Teller effect, forming vibronic states. These Jahn-Teller active modes are responsible for the isotope shift. In this case $\partial E/\partial\hbar\omega_i$ becomes smaller than $g/2$ for the vibronic ground state [3]. The Fe³⁺ and Ni³⁺ systems are Jahn-Teller active only in the excited ⁴T₁ and ⁴T₂ state whereas the ⁶A₁ and ⁴A₂ ground states are non Jahn-Teller active. For the Cu²⁺-

out that the observed intensity ratio of the satellite ZPLs (b, c) agrees well with the probability of the different (TM-O₄)-clusters (Fig. 4). In conclusion it seems to be unambiguous from these statistical considerations in combination with the observed intensity ratios, to attribute the satellite lines to isotope shifts within the (TM-O₄)-cluster where one of the four ¹⁶O-ligands is replaced by a ¹⁸O-atom.

5) DISCUSSION

Now the observed isotope shifts are discussed in terms of equation 2. First, we start with the discussion of the phonon mass dependence $\partial\hbar\omega_i/\partial M$.

The summation (eq. 2) includes the whole phonon system, but only the mass-dependent local phonon modes ($\partial\hbar\omega_i/\partial M \neq 0$) give nonvanishing contribution. A strong mass dependence is expected for strongly localized modes, i. e. modes appearing in the density of states gap of the perfect lattice. The mass dependence of the local phonon modes can be calculated within the Keating valence force model using local mode energies experimentally determined, e. g. by Raman-spectroscopy.

transition the situation is different because both the 2T_2 -ground and the 2E -excited states are Jahn-Teller active but T_2 -modes couple only to the 2T_2 -ground state in first order. Now the sign of the isotope shifts can be explained because for Ni^{3+} and Fe^{3+} the mass dependence of the Jahn-Teller active excited states is smaller than of the non Jahn-Teller active ground states, whereas for copper the situation is vice versa. The sign of the ligand induced isotope shift agrees in all cases with that of the TM one but the order of magnitude is larger. There are many possible reasons to account for this effect. First, all local phonons (A_1 , E , T_1 , T_2) move the ligands and this gives a larger contribution in the sum of eq. 2, if they are Jahn-Teller active. Secondly, the relative mass difference is larger for oxygen ($\sim 6\%$ /nucleon) than for iron ($\sim 1.8\%$ /nucleon) nickel ($\sim 1.7\%$ /nucleon) and copper ($\sim 1.6\%$ /nucleon). It should be pointed out that the dominant contribution in the mass dependence results from the local phonon modes, which move the ligands strongest. Especially local optical modes in the 50-70meV region are responsible for the largest oxygen-movement. These phonon-modes are observed in the vibronic spectra of the slighter Jahn-Teller active states. This is in full agreement with the stronger mass dependence of these states (eq. 2). The shift, induced by the inequivalent lattice site of the oxygen-ligand (Fig. 4), is probably caused by the influence of the trigonal crystal field on the Jahn-Teller effect. As the E-mode coupling is strongest in $ZnO:Fe^{3+}$, the inequivalent lattice site splitting is largest. For $ZnO:Cu^{2+}$ and Ni^{3+} the T_2 -mode coupling is stronger, resulting in a smaller oxygen-induced inequivalent lattice site isotope splitting.

5) CONCLUSION

The presented results give new insight into the local vibrational system of TM centers and the electron-phonon interaction. It is pointed out that the sign of the isotope shift is mainly determined by the Jahn-Teller effect and that the order of magnitude is influenced by the local phonon contribution. In general, the ligand induced isotope shift is an inevitable inhomogeneous ZPL broadening mechanism in TM doped semiconductors. However, ZnO is very suitable for detailed studies, as the relative differences in mass and abundance between the stable oxygen-isotopes are large and the FWHM of the ZPLs is in the order of just $30\mu eV$.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. G. Heiland and Prof. E. Mollwo for supplying the high quality ZnO crystals.

REFERENCES

- [1] A. Hoffmann, U. Scherz, *J. Crystal Growth* 101 (1990) 385
- [2] G. F. Imbush, W. M. Yen, A. L. Schalow, G. E. Devlin and J. P. Remeika, *Phys. Rev.* 134 (1964) A481
- [3] B. Nestler, A. Hoffmann, L. B. Xu, U. Scherz, I. Broser, *J. Phys. C* 20 (1987) 4613
- [4] R. E. Dietz, H. Kamimura, M. D. Sturge, A. Yariv, *Phys. Rev.* 132 (1963) 1559
- [5] P. Thurian, R. Heitz, A. Hoffmann, I. Broser, *J. Crystal Growth* 117 (1992) 727
- [6] R. Heitz, A. Hoffmann, I. Broser, *Phys. Rev. B* 45 (1992) 8977
- [7] T. Yamaguchi, H. Kamimura, *J. Phys. Soc. Japan* 33, 4 (1972) 953
- [8] I. Broser, A. Hoffmann, R. Heitz, P. Thurian, *J. of Lum.* 48/49 (1991) 693
- [9] B. M. Kimpel, H.-J. Schulz, *Phys. Rev. B* 43 (1991) 9938
- [10] P. Thurian, R. Heitz, T. Jentsch, A. Hoffmann, I. Broser, *Physica B* 185 (1993) 239
- [11] A. Hoffmann, R. Heitz, I. Broser, *Phys. Rev. B*, 41, 9 (1990) 5806
- [12] S. V. Melnichuk, V. I. Sokolov, T. P. Surkova, V. M. Chernov, *Sov. Phys. Solid State* 33 (11) (1991) 1833