

Low-Frequency Raman Spectrum of Bulk $\text{Zn}_{0.984}\text{Co}_{0.016}\text{O}$ Crystal

W. SZUSZKIEWICZ^{a,*}, A. ŁUSAKOWSKI^a, J.F. MORHANGE^b, Z. GOŁACKI^a, M. ARCISZEWSKA^a,
B.B. BRODOWSKA^a, M. KANEHISA^b, M. KLEPKA^a AND W. DOBROWOLSKI^a

^aInstitute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warszawa, Poland

^bInstitut des Nanosciences de Paris, UPMC, CNRS UMR 7588, 140 rue de Lourmel, 75015 Paris, France

The influence of possible presence of Co^{2+} ion pairs in a bulk $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystal on the low-frequency part of the Raman spectrum is discussed. Two effects can be taken into account in the theoretical considerations when analyzing the energy level scheme corresponding to Co ions. The first is a local lattice deformation in the vicinity of Co^{2+} ion due to a presence of the second ion, smaller than the host ZnO lattice cation. Such deformation creates a trigonal field, which can only slightly modify the energy levels of Co^{2+} ion. The second effect, which results from an antiferromagnetic superexchange interaction between two Co^{2+} ions is responsible for a new set of energy levels. The Raman data taken at low temperature on the sample corresponding to the composition $x = 0.016$ demonstrated the presence of two structures at about 6 cm^{-1} and 13 cm^{-1} . These structures may be interpreted as electronic transitions between the ground state and the first excited state of a single Co^{2+} ion in the substitution site of ZnO lattice and as a similar transition for Co^{2+} ion pair, respectively.

PACS numbers: 75.50.Pp, 78.30.Fs

1. Introduction and motivation

The diluted magnetic semiconductors (DMS) attract a strong research interest because of their potential applications in spintronics. Since the prediction of room temperature ferromagnetism (RTFM), arising from carrier-mediated exchange interactions for some transition metal (TM) doped ZnO [1, 2], the physical properties of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals have been the object of extensive studies. However, in spite of huge experimental effort, results of measurements of the magnetic properties of similar systems are often controversial and the situation, up to now, remains unclear. As it is believed, the principal reason for the observed difference in the magnetic behavior of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals is a possible presence of secondary (magnetic) phases and/or complex defects that influence magnetic properties of analyzed samples. A presence of several antiferromagnetic or ferromagnetic precipitates in the mixed crystals under consideration like, e.g., cobalt clusters, different cobalt oxides or various $\text{Zn}_{1-x}\text{Co}_{2+x}\text{O}_4$ spinels have been reported in many papers. A variety of experimental techniques (X-ray diffraction, Raman scattering, electron diffraction, X-ray absorption fine structure, X-ray magnetic circular dichroism, etc.) have been applied in order to detect different secondary phases in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals.

According to widely accepted opinion confirmed by numerous experimental data, most or even almost all cobalt ions occupy substitutional (Zn) sites in the host crystal lattice and are in the Co^{2+} charge state (see e.g. [3–7] and references therein). The principal exchange interaction mechanism between such Co^{2+} ions (without a huge concentration of free carriers) is an antiferromagnetic superexchange. Due to two different possible neighborhoods of Co^{2+} ions in ZnO one can expect two different values of the exchange integral J that describes the interaction between the nearest neighbors. Only a few experimental and theoretical papers estimate the value of such integral corresponding to the stronger antiferromagnetic interaction between the nearest neighbors [8–12]. All these values are spread out between -9 K and -41 K , the most precise and relatively recent data suggest a value J close to about -21 K [12].

While the RTFM observed in some $\text{Zn}_{1-x}\text{Co}_x\text{O}$ samples has been typically attributed to the creation of magnetic states around zinc vacancies and/or of complex defects containing Co^{2+} ions [13–16], some papers suggested also a formation of small Co clusters as a possible cause of this effect.

The Raman scattering started on $\text{Zn}_{1-x}\text{Co}_x\text{O}$ a few years ago. Most of the measurements were performed at room temperature only ([17] and references therein, see also [14, 18, 19]), the low-frequency spectral range has not attracted a lot of attention up to now [17]. A large number of experimental data for the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals confirm the substitution position of Co^{2+} ion in

* corresponding author; e-mail: szusz@ifpan.edu.pl

the host ZnO lattice as well as the presence of various types of precipitates in such system. Much more limited experimental information concerning both possible non-random Co^{2+} ions distribution in the crystal lattice (e.g., ion clustering) and creation of complex defects in ZnO (like, e.g., an oxygen vacancy in the vicinity of Co^{2+} ion) is available. The goal of the present work is to analyze a possible influence of a presence of Co^{2+} ion pairs on the TM energy levels and, in particular, on the electronic transitions between the TM energy ground state and first excited levels.

2. Experimental

For the growth of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals with the nominal composition $x \leq 0.05$, the chemical vapor transport (CVT) method was applied. The crystals were grown at the Institute of Physics, PAS, in Warsaw at about 1050–1100 °C in Zn-rich conditions, the reactive (Br, Cl) gases present inside closed quartz ampoules supported the transport of dopant. The bulk sample containing approximately 1.6 at.% of Co [17] has been selected for a further analysis with the use of the Raman spectroscopy. The total Co content in the investigated sample was determined by two independent methods: by the electron microprobe and by measurements of magnetic properties (from the saturation of magnetization). Both methods gave similar results.

Raman scattering measurements were performed using a Jobin-Yvon U1000 double monochromator in the vicinity of the laser excitation line (in the spectral range from about -30 cm^{-1} to 30 cm^{-1}) with a spectral resolution slightly above 1 cm^{-1} . The 488 nm Ar^+ laser line was applied for the excitation, a photon counting system and a S20 photomultiplier served as the detector system. To achieve low-temperature measurements the sample was placed on the cold finger of a continuous-flow helium cryostat, the lowest sample temperature was estimated as equal to about 20 K. Because of the irregular shape of the sample, no polarization studies were attempted, but to increase the stray light rejection, the spectrum was taken in a crossed polarization configuration (polarization of the scattered light was perpendicular to the polarization of the incident light). Both Stokes and anti-Stokes parts of the spectrum were recorded in order to check the Raman nature of the peaks.

3. Results and discussion

Figure 1 shows a Raman spectrum taken at $T = 20 \text{ K}$ on a Co-doped ZnO sample containing about 1.6 at.% of Co in a narrow spectral range in close vicinity of the laser excitation line. Because the stray light at the origin somehow obscures the observation in the spectral range below 10 cm^{-1} , a Rayleigh scattering (dashed line) has been simulated by the sum of a Gaussian curve and a Lorentzian line centered at 0 cm^{-1} . The result of such simulation has been superposed to a straight line slightly

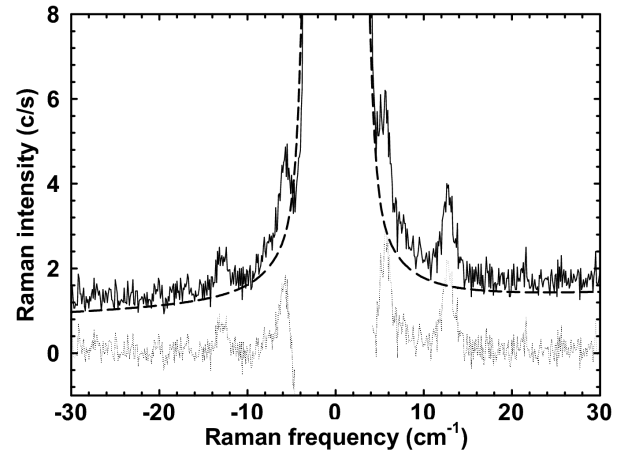


Fig. 1. Low-temperature Raman spectrum taken on the ZnO sample containing about 1.6 at.% of Co in the vicinity of the Ar^+ laser line ($T = 20 \text{ K}$, $\lambda = 488 \text{ nm}$, laser line power 50 mW). Solid line corresponds to the experimental spectrum, dashed line is a simulated background, taking into account the Rayleigh scattering, and dotted line corresponds to the subtraction of these two lines.

inclined, representing all the background in the low frequency region. The subtraction of this function from the accumulated spectrum is shown by the dotted line in Fig. 1.

The well-defined structure can be observed at about 13 cm^{-1} as well as another one on the side of the Rayleigh line near 6 cm^{-1} . A possible shoulder is also merely observable near 7 cm^{-1} but this effect still requires a confirmation by the Raman scattering measurements, performed with higher spectral resolution.

Considering the very low energy of these peaks, it is tempting to attribute them to electronic transitions between splitted electronic levels. The energy distance between the ground state and the first excited state of the Co^{2+} ion has been previously studied either theoretically [20, 21] or by far-infrared EPR spectroscopy [6]. According to the literature data, the value of 5.5 cm^{-1} corresponds to the splitting of the Co^{2+} ion ground state in the ZnO lattice due to the spin-orbit interaction. The structure, observed close to that frequency in the Raman spectrum, confirms in a direct manner the local trigonal symmetry of the site occupied by an isolated Co^{2+} ion in the crystal lattice.

The second structure observed at about 13 cm^{-1} cannot be attributed to electronic transitions between energy levels of an isolated Co^{2+} ion because of the lack of possible candidate for such transitions according to the energy level scheme known from the literature. As it has been demonstrated previously by Raman scattering measurements performed in a much wider spectral range [17], the investigated sample contains both Co and CoO precipitates. None of these secondary phases exhibit any vibration, electronic, or magnetic excitations that may

be the origin of the observed Raman signal at the frequency given above. The temperature dependence of the structure at 13 cm^{-1} suggests that it is not due to lattice excitations and probably have a magnetic origin because it disappears at higher temperature.

To explain this structure, we have calculated the energy levels of pair of Co^{2+} ions in a substitution position in the ZnO lattice, using the following method. The energies of the excited states of Co^{2+} ion in a deformed environment have been calculated using point charge model with properly fitted parameters. First, in order to obtain positions of cobalt ion and the surrounding oxygen anions in ZnO host lattice, the *ab initio* calculations have been performed using OpenMX package [22]. The LDA pseudopotentials, $2 \times 2 \times 2$ supercell, and 150 Ry energy cutoff have been applied. In the case of Co^{2+} pairs, $3 \times 2 \times 2$ supercells were used. After a geometry optimization procedure, an information about the relative positions of all the above mentioned ions and the local lattice distortion was obtained. Such information has enabled, using the point charge model, theoretical calculations of the Co^{2+} ion energy spectrum in a deformed lattice environment resulting from the presence of the second ion in a close vicinity of the first one. In addition to the modifications of Co^{2+} ion's energy levels caused by local lattice deformations, we have also calculated the influence of the antiferromagnetic exchange interaction on the energy spectrum of Co^{2+} nearest neighbor pair.

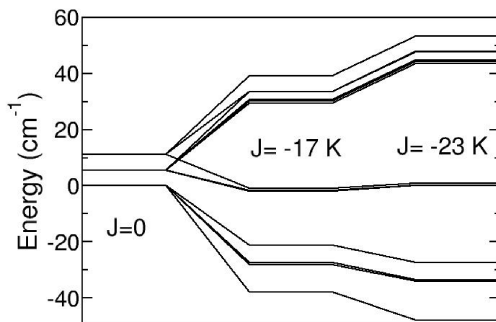


Fig. 2. The lowest energy levels corresponding to the pair of Co^{2+} ions in ZnO lattice calculated for a few values of the exchange integral J , describing an antiferromagnetic exchange between the nearest Co^{2+} neighbors.

Figure 2 presents the lowest energy levels of Co^{2+} ion pair placed in ZnO lattice, calculated for a few different values of the exchange integral J corresponding to a superexchange interaction between the magnetic nearest neighbors. As one can see, there exists a perfect coincidence between the expected energy of the first electronic transition for such system (located in the range between about 12 cm^{-1} and 15 cm^{-1}) and the position of the higher frequency structure observed in the Raman spectrum.

Results of the present calculations also demonstrate that a modification of the Co^{2+} first excited level energy

induced by the local deformation of the crystal lattice, resulting from replacement of the Zn ion by the Co ion in a close neighborhood of the Co^{2+} ion under consideration is not very significant. However, this is simply due to the similar size of both cations. The ionic radii of Zn^{2+} ion and Co^{2+} ion are equal to 0.60 \AA and 0.58 \AA , respectively [23].

If the interpretation of the structure located at about 13 cm^{-1} presented in this paper is correct, it is the first observation of the electronic transition between the ground state and the excited state of TM ion pair in DMS by an optical measurement. Further studies are required to strengthen our interpretation of the Raman spectrum presented in this paper. For example, still larger effects can be expected when analyzing the possible influence of the presence of other ions of different size than those corresponding to Zn^{2+} and Co^{2+} ions. As it has been mentioned previously, the local lattice deformation resulting from a presence of zinc vacancy (or a complex defect) in the vicinity of the analyzed Co^{2+} ion was suggested in several recent papers devoted to the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ system. The influence of this effect on the optical spectra of this material also requires further studies.

4. Conclusions

Our analysis shows that possible presence of Co^{2+} ion pairs in highly Co-doped ZnO crystals and/or the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ mixed crystals may modify in a noticeable manner the scheme of the energy levels corresponding to the TM in a substitution site and influence the optical properties of the material under consideration. The results of theoretical calculations demonstrate that an additional local deformation of the crystal lattice in the vicinity of Co^{2+} ion, due to a presence of the second ion and resulting from the size difference between Zn^{2+} and Co^{2+} ions can slightly modify the set of Co^{2+} energy levels. Due to an antiferromagnetic superexchange interaction between the nearest Co^{2+} neighbors, present at low temperatures, some new optical transitions, taking place in a system of Co^{2+} ion pairs, may also be expected. The low-frequency Raman spectrum, taken on $\text{Zn}_{0.984}\text{Co}_{0.016}\text{O}$ mixed crystal at $T = 20\text{ K}$ in a close vicinity of the laser line can be interpreted as an experimental evidence of both effects mentioned above. More experimental data are clearly required in order to confirm the present interpretation of the spectrum and to get more detailed information about the mechanisms that influence the TM energy levels.

Acknowledgments

The research was partially supported by the Ministry of Science and Higher Education (Poland) through Grant No. N515 015 32/0997, the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08), and by the POLONIUM project 7011/R07/R08.

References

- [1] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, *Science* **287**, 1019 (2000).
- [2] K. Sato, H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* **39**, L555 (2000).
- [3] S. Deka, P.A. Joy, *Solid State Commun.* **134**, 665 (2005).
- [4] M. Millot, J. Gonzalez, I. Molina, B. Salas, Z. Golacki, J.M. Broto, H. Rakoto, M. Goiran, *J. Alloys Comp.* **423**, 224 (2006).
- [5] S. Deka, R. Pasricha, P.A. Joy, *Phys. Rev. B* **74**, 033201 (2006).
- [6] P. Sati, R. Hayn, R. Kuzian, S. Régnier, S. Schäfer, A. Stepanov, C. Morhain, C. Deparis, M. Laügt, M. Goiran, Z. Golacki, *Phys. Rev. Lett.* **96**, 017203 (2006).
- [7] A. Ney, K. Ollefs, S. Ye, T. Kammermeier, V. Ney, T.C. Kaspar, S.A. Chambers, F. Wilhelm, A. Rogalev, *Phys. Rev. Lett.* **100**, 157201 (2008).
- [8] S. Kolesnik, B. Dabrowski, J. Mais, *J. Appl. Phys.* **95**, 2582 (2004); *Phys. Status Solidi C* **1**, 900 (2004).
- [9] M.H. Sluiter, Y. Kawazoe, P. Sharma, A. Inoue, A.R. Raju, C. Rout, U.V. Waghmare, *Phys. Rev. Lett.* **94**, 187204 (2005).
- [10] L.M. Sandratskii, P. Bruno, *Phys. Rev. B* **73**, 045203 (2006).
- [11] T. Chanier, M. Sargolzaei, I. Opahle, R. Hayn, K. Koepernik, *Phys. Rev. B* **73**, 134418 (2006).
- [12] P. Sati, C. Deparis, C. Morhain, S. Schäfer, A. Stepanov, *Phys. Rev. Lett.* **98**, 037204 (2007).
- [13] C.H. Patterson, *Phys. Rev. B* **74**, 144432 (2006).
- [14] C. Sudakar, P. Kharel, G. Lawes, R. Suryanarayanan, R. Naik, V.M. Naik, *J. Phys., Condens. Matter.* **19**, 026212 (2007).
- [15] T. Chanier, I. Opahle, M. Sargolzaei, R. Hayn, M. Lannoo, *Phys. Rev. Lett.* **100**, 026405 (2008).
- [16] Q. Wang, Q. Sun, G. Chen, Y. Kawazoe, P. Jena, *Phys. Rev. B* **77**, 205411 (2008).
- [17] W. Szuszkiewicz, J.F. Morhange, Z. Gołacki, A. Lusakowski, M. Schumm, J. Geurts, *Acta Phys. Pol. A* **112**, 363 (2007).
- [18] H. Zhou, L. Chen, V. Malik, C. Knies, D.M. Hofmann, K.P. Bhatti, S. Chaudhary, P.J. Clar, W. Heimbrod, C. Klingshirn, H. Kalt, *Phys. Status Solidi A* **204**, 112 (2007).
- [19] M. Schumm, M. Koerdel, J.F. Morhange, Z. Gołacki, K. Graszka, P. Skupinski, W. Szuszkiewicz, H. Zhou, V. Malik, H. Kalt, C. Klingshirn, J. Geurts, *J. Phys., Conf. Series* **92**, 012149 (2007).
- [20] P. Koidl, *Phys. Rev. B* **15**, 2493 (1977).
- [21] H.-J. Schulz, M. Thiede, *Phys. Rev. B* **35**, 18 (1987).
- [22] See <http://www.openmx-square.org> .
- [23] R.D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).