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Raman spectroscopy of $Zn_{1-x}Co_xO$ bulk mixed crystals

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We report on a study of structural properties of $Zn_{1-x}Co_xO$ by micro- and macro-Raman scattering from phonons. Bulk mixed crystals ($x \le 0.03$), grown by chemical vapour transport were investigated between 5 K and 295 K. Beside the common eigenmodes of the ZnO host lattice, we observed disorder-induced lattice vibration modes and a structure, tentatively assigned to a local vibration mode of the Co impurity. Our results are compared with literature data of other ZnO-based diluted magnetic semiconductors such as (Zn,Mn)O.

Key words: *$Zn_{1-x}Co_xO$; Raman scattering; lattice vibrations; diluted magnetic semiconductor*

1. Introduction and motivation

In recent years, diluted magnetic semiconductors (DMS) have attracted interest for their potential application in future spin-based electronics (spintronics) [1]. Among these materials, DMSs based on ZnO play a prominent role since room temperature ferromagnetism (RTFM) arising from carrier-mediated exchange interactions has been predicted for several transition metal doped ZnO (ZnO:TM) [2, 3]. One of these promising materials is the mixed crystal $Zn_{1-x}Co_xO$.

Many studies on the magnetic properties of $Zn_{1-x}Co_xO$ have been performed until now but their results were often ambiguous or even contradictory. The magnetic properties of this material depend on the conditions during the crystal growth and also on the sample type (bulk crystal, thin layer, ceramic sample, nanocrystal, or nanowire) and on the after-growth treatment (e.g. annealing). In the case of polycrystalline bulk $Zn_{1-x}Co_xO$ samples prepared by solid state reaction method, most of them exhibited

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a paramagnetic or even antiferromagnetic behaviour at room temperature (RT). The RTFM observed in some other samples was attributed either to the generation of oxygen vacancies or the appearance of Co clusters. Similar explanations (or the formation of secondary phases containing Co) were proposed for bulk polycrystalline ferromagnetic samples prepared by other methods. Experimental reports of RTFM in selected $Zn_{1-x}Co_xO$ films have further intensified the interest in this system. Nevertheless, in spite of numerous investigations, a general understanding of its magnetic properties is still missing.

There is a general agreement that a key question for the understanding of all these results is whether the material contains only randomly distributed TM ions at the substitutional position in the host crystal lattice or if the material under interest contains also (mostly?) clusters, precipitates or secondary phases that are responsible for the observed magnetic properties [4–7].

One of the possible experimental methods to study the structure properties of materials is Raman spectroscopy. Raman scattering studies on $Zn_{1-x}Co_xO$ system started very recently, all forms of possible samples were analyzed (see, e.g., [8–13] and references therein). All but one ([10]) papers were limited to micro-Raman studies on samples with composition varying from the Co content below $x = 0.01$ up to $x = 0.20$ in an extreme case. Most measurements were performed at RT only, without any polarization analysis of the recorded spectra. The presence of such precipitates as Co ($x = 0.05$, [9]) and/or various cobalt oxides or cobalt spinel ($x > 0.05$, [11]) has been found (or at least suggested) for selected (not all) samples when the mixed crystal composition exceeds at least $x = 0.03$. Several local vibrational modes (LVMs) are expected for a transition metal impurity occupying a substitutional site in the hexagonal crystal lattice (see, e.g., [14, 15]). However, in spite of numerous experimental efforts, expected sharp structures, resulting from the LVMs of Co, have not been observed in the Raman spectra until now.

The goal of the present work is to get information about the position of the Co ions in the ZnO crystal lattice and about the overall crystal structure by analysing the lattice dynamics. Raman spectroscopy and bulk $Zn_{1-x}Co_xO$ samples corresponding to $x \leq 0.03$ have been selected for this purpose.

2. Experimental

For the growth of the $Zn_{1-x}Co_xO$ crystals, the chemical vapour transport (CVT) method was applied. The crystals were grown at about 1050–1100 °C in Zn-rich conditions. Both inert (Ar, N_2) and reactive (Br, Cl) gases supporting the transport of dopants were used in the growth system. Pure ZnO crystals were grown both in Zn-rich and stoichiometric conditions, part of them was annealed in oxygen after the growth. More details can be found, e.g., in [10].

Due to a similarity of the atomic masses of Co and Zn one cannot expect a significant evolution of the parameters describing phonon modes with changing mixed crystal composition, at least for the very narrow composition range analyzed in this paper.

Under these circumstances, only two types of samples have been considered: slightly Co-doped ZnO crystals (with x well below 0.01) and real mixed crystals, nominally containing a few percent of Co (but corresponding to the composition for which possible presence of neither pure Co nor cobalt spinel has been reported). Pure ZnO crystals were also grown for a comparison. The structure quality of the selected crystals grown by the method described was previously checked by the X-ray diffraction (not reported here), a possible presence of other phases was not detected by this method.

Typical Raman scattering measurements were performed using a Jobin–Yvon U1000 double monochromator in the spectral range from 300 cm^{-1} to 650 cm^{-1} with the spectral resolution close to 1 cm^{-1}. The Ar^+ laser lines of the wavelengths 514.5 nm or 476.5 nm were applied for the excitation. A Peltier effect cooled photon counting system and S20 photomultiplier served as the detector system. For the low-temperature measurements, the sample was placed on the cold finger of a continuous-flow helium cryostat, the sample temperature was estimated to be about 15 K. Because the bulk samples were polycrystalline or not oriented, no polarization analysis of the Raman scattering has been performed.

The micro-Raman measurements with the use of the microscope were performed on selected samples both at RT and at 5 K. The 514.5 nm Ar^+ laser line was applied for the excitation. The light was focused on the sample surface by a 80× ULWD microscope objective, the scattered light was analysed by a triple monochromator (Dilor XY, focal length 500 mm), and accumulated with a liquid-nitrogen cooled CCD-array detector.

3. Results and discussion

Figure 1 shows the Raman spectra taken at RT with two experimental set-ups on pure ZnO and two Co-doped ZnO samples with a low Co content. The upper panel and the lower panel show the macro-Raman spectra, the micro-Raman data are shown in the middle. A non-oriented sample has been used for these measurements hence the relative intensities of the principal peaks are slightly different. The band near 335 cm^{-1} can be interpreted as a double phonon corresponding to the subtractive combination of the E_2 (high) mode at 438 cm^{-1} and the E_2 (low) mode at 100 cm^{-1}.The three structures observed in the middle correspond to typical and well known first order host lattice modes, namely to A_1 (TO) 378 cm^{-1}, E_1 (TO) 410 cm^{-1}, and E_2 (high) 438 cm^{-1}, respectively. The numerical values of frequencies given above are typical ones but can vary, as the frequencies of various extraordinary phonons change with the orientation in an uniaxial material. The mode with the maximum at about 539 cm^{-1} is only observed in Co doped ZnO, and can thus been interpreted as an impurity mode or at least a disorder induced one. The presence of additional modes (or band) in the spectral region between 500 cm^{-1} and 600 cm^{-1} was reported previously not only for $Zn_{1-x}Co_xO$, but also for ZnO containing other dopants, like Mn (see, e.g., [10, 16]) or Ti [16]. On the other hand, modes in this spectral range are not clearly observed on $Zn_{1-x}Co_xO$ films with a high Co content [13] or on Co-doped ZnO nanowires [12]. The presence of the

B_1 (high) silent mode in this area (at 552 cm^{-1}) has also been predicted by theoretical calculations [17], the A_1 (LO) and E_1 (LO) modes of pure ZnO are expected in the spectral range 575–585 cm^{-1}. All modes listed above may contribute to the total intensity of the broad band observed experimentally.

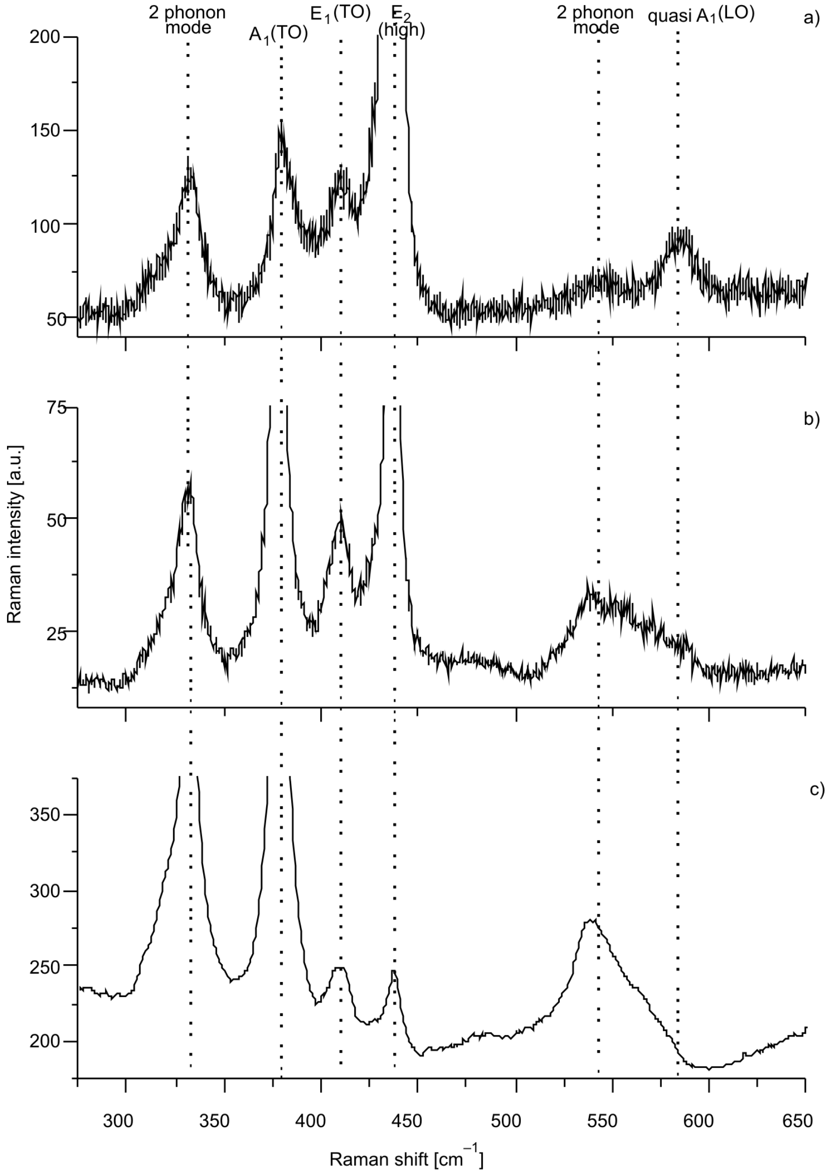

Fig. 1. Raman spectra taken at RT with the Ar^+ (514.5 nm) laser line as the excitation source on ZnO sample (a) and on two as-grown, slightly Co-doped ZnO crystals taken under the microscope (b) and the macro-Raman spectrum (c); for the discussion of the origin of observed modes see the main text

Figure 2a, b shows macro-Raman spectra taken at 15 K on annealed in oxygen pure ZnO and on the $Zn_{1-x}Co_xO$ mixed crystal (with $x \approx 0.03$), respectively. The observed high intensity of both peaks may result form the particular crystal orientation and from a noticeable non-stoichiometry. The lowest panel corresponds to the micro-Raman spectrum taken at 5 K for the $Zn_{1-x}Mn_xO$ mixed crystal ($x \approx 0.01$). The sharp structure corresponding to the best known and usually observed LVM of the Mn impurity is indicated in this figure.

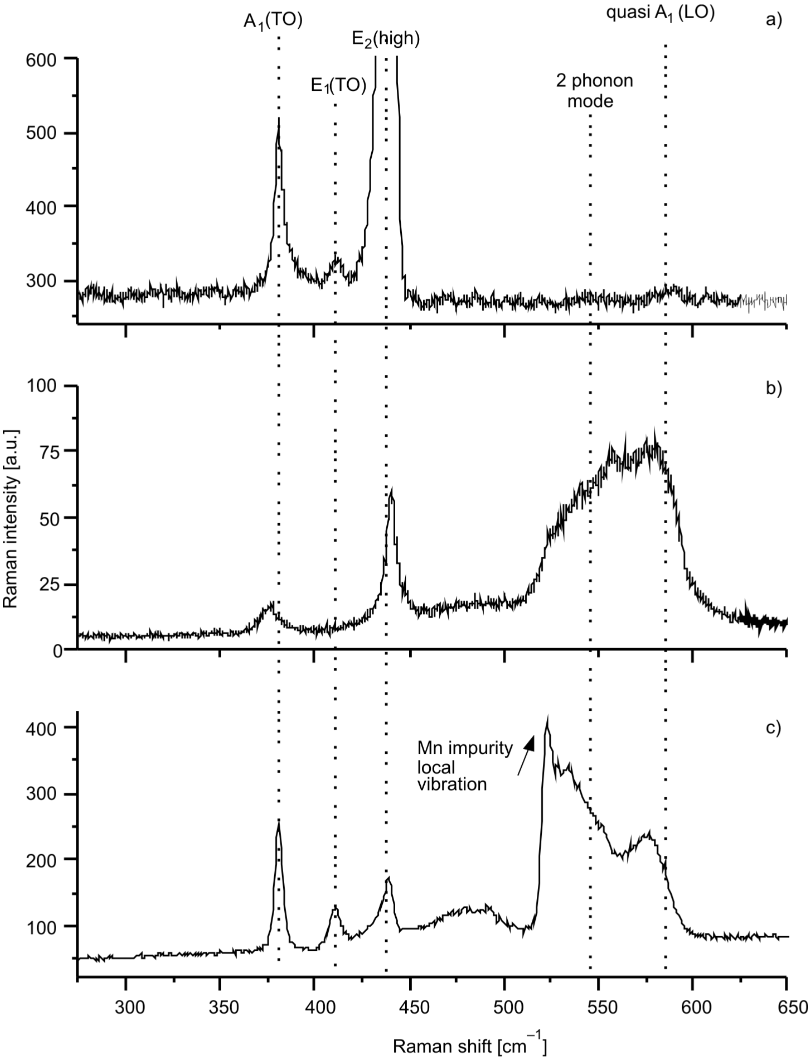

Fig. 2. Raman spectra taken at low temperatures: a) pure ZnO annealed in oxygen after growth, macro-Raman, 15 K, b) $Zn_{1-x}Co_xO$ mixed crystal ($x \approx 0.03$), macro-Raman, 15 K, c) $Zn_{1-x}Mn_xO$ mixed crystal ($x \approx 0.01$), micro-Raman, 5 K; Ar^+ (476.5 nm) laser excitation has been used for pure ZnO, the same excitation line as that applied at RT (Fig. 1) was used for transition metal doped crystals (details in the text)

The additional structure observed at 333 cm^{-1} is due to the second order Raman scattering. The intensity of this structure may be enhanced due to the crystal disorder. Some differences in the host lattice modes intensity ratio and the disappearance of the E_1 (TO) mode results from different crystal orientations, as well as their slight frequency shift which is probably due to the “extraordinary” nature of some phonons in a uniaxial material as noted above. Some differences in the form of the broad bands in the spectral range between 500 cm^{-1} and 600 cm^{-1}, presented in Fig. 1 and Fig. 2, may be observed. A similar modification of the form of this band with an increasing Co content in the mixed crystal can be found in some literature data concerning this system.

It should be stressed that, while in the case of $Zn_{1-x}Mn_xO$ mixed crystals several research groups observed and identified LVMs of Mn (or Mn-related complex) in ZnO and for one of these modes a really sharp structure has been observed at low temperatures (see, e.g., [10, 16] and Fig. 2) a similar vibration with well determined frequency is not observed for $Zn_{1-x}Co_xO$. Some additional small structures observed in the spectral range of interest can always be interpreted in another manner. The only exception could be a not very well pronounced structure at about 556 cm^{-1} at low temperatures on the samples containing a few percent of Co. This structure does not appear neither in pure ZnO nor in $Zn_{1-x}Mn_xO$ mixed crystals. Moreover, the form of the band observed on the $Zn_{1-x}Co_xO$ samples cannot be explained by a selected, high-frequency host lattice modes and some combinations of other lattice modes resulting form the ZnO lattice vibrations only.

Several authors analyzing magnetic properties of ZnO-based DMS point to a difference between doping with Mn and Co (e.g., [18]) and stress a sensitivity of a given DMS magnetic behaviour to the transition ion neighbourhood in the crystal lattice. Up to our knowledge, a detailed analysis of the local symmetry of Co^{2+} ions is possible only for a low composition range [19] where possible sharp local impurity vibrations cannot be observed. We believe that a proper explanation of the observed Raman spectra (both our and the literature data) could be the following. With an increasing Co content in $Zn_{1-x}Co_xO$, isolated Co^{2+} ions in the mixed crystal are replaced by a complex (containing, e.g., another Co^{2+} ion, an oxygen vacancy, a zinc interstitial, or a hydrogen ion) leading to a local deformation of the lattice. In particular, according to the literature, the Co-related complex may be not as simple as that corresponding to Mn dopant in ZnO. Due to different possible orientations of such complexes and because of interactions between the ions, one could expect a broadening of the local vibration mode and observe a rather broad band instead of finite frequencies for such excitations. Under these circumstances, the observed form of the vibration band could be considered as an optical evidence of a complex containing the Co^{2+} ion.

One should mention that mostly as-grown $Zn_{1-x}Co_xO$ samples were investigated in the present paper. As is well known, post-growth annealing may modify the mixed crystal stoichiometry, type and density of defects, possible precipitates etc. The possible influence of oxygen vacancies and Zn interstitials on the Raman spectrum has been mentioned in a few papers but more systematic studies of this kind are clearly required. Results of such investigations should finally explain the origin of the variety of observed properties of different $Zn_{1-x}Co_xO$ samples with nominally similar chemical compositions.

4. Conclusions

So far, experimental reports on ferromagnetism in $Zn_{1-x}Co_xO$ have been controversial and seem to be sensitive to sample preparation and to post-growth treatment (like, e.g., annealing). It is very probable that precipitates of other Co-related crystal phases or clustering of the magnetic ions into an impurity phase might be responsible for such features. In spite of these controversies, $Zn_{1-x}Co_xO$ is believed to be the best candidate for room temperature ferromagnetism among the TM-doped ZnO family. The present Raman spectra taken at frequencies above 300 cm^{-1} on bulk mixed crystals (containing not more than 1% and a few percent of Co, respectively) do not indicate a possible presence of additional crystal phases. However, the analysis of Raman scattering spectra suggests that they cannot be simply due to the presence of this element at the substitutional site of the cation sublattice. It is very probable that a replacement of Zn by Co ion is accompanied by a local lattice distortion and/or the creation of a complex defect. Various complexes (containing, e.g., another cobalt ion, a zinc atom at the interstitial position, oxygen vacancy, or a hydrogen atom) have been previously proposed. The suggested interpretation of Raman scattering spectra is confirmed by a difference seen in the comparison of the presented results with the literature data, corresponding to $Zn_{1-x}Mn_xO$. In the latter case, a few LVMs (and among them at least one really "sharp" with a well defined frequency) have been observed in the lattice dynamics by a few research groups. More experimental data (in particular, taken on annealed and as-grown samples in a lower frequency region) are clearly required in order to get more information about the nature of complexes, involved in the creation of room temperature ferromagnetism.

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