Magnetic ordering in $Co_cMg_{1-c}O$ solid solutions

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The influence of dilution by diamagetic ions on the magnetic ordering in single-crystal $Co_cMg_{1-c}O$ solid solutions was studied by Raman spectroscopy and magneto-optical microscopy in a wide range of temperatures ($6 < T < 200$ K). Far infra-red absorption measurements of antiferromagnetic resonance (AFMR) were also performed for pure CoO. It was found that the domain structure and the contribution from Brillouin zone center magnons to Raman scattering and AFMR disappear well below the Néel temperature, determined by neutron diffraction and magnetic susceptibility measurements.

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1. Introduction

$Co_cMg_{1-c}O$ system is a nice example of diluted antiferromagnet [1,2]. It forms a continuous series of solid solutions, whose magnetic properties vary with the composition from antiferromagnetic-like behaviour with the Neél temperature $T_N = 290$ K for pure CoO to diamagnetic-like for pure MgO. For intermediate compositions with $c > 0.5$, the paramagnet-to-antiferromagnet phase transition occurs upon cooling. Note that paramagnetic CoO has the NaCl-type crystal structure (space group $Fm3m$), and the antiferromagnetic ordering is associated with a cubic-to-monoclinic transition (space group $C2/m$ with two CoO units per cell) [3].

In this we report the results of the Raman spectroscopy studies and micscopic magneto-optical observations of domain structure in single-crystal $Co_cMg_{1-c}O$ solid solutions performed in a wide range of temperatures ($6 < T < 200$ K). The far infra-red (IR) measurements of antiferromagnetic resonance (AFMR) and magnetic Raman scattering in pure single-crystal CoO are used for comparison.

2. Experimental

The $Co_cMg_{1-c}O$ samples used in the present work were single-crystals from polycrystalline solid solutions by the method of chemical transport reaction (the „sandwich“ technique) on the (100) face of MgO single-crystals. Polycrystalline $Co_cMg_{1-c}O$ solid solutions were prepared using technology from the appropriate amounts of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ salts, which were mixed and slowly evaporated. The remaining dry „flakes“ were heated up to 500–600°C to remove NO_2 completely. The obtained polycrystalline solid solutions were pressed and annealed during 100 h at 1200°C in air and then repidly cooled down to room temperature.

Far-IR optical absorption measurements were performed at SINBAD Beamline of the DA FNE synchrotron radiation source (Frascati, Italy) using the Brucker Equinox 55 interferometer, modified to work in vacuum in the far-IR with a liquid He-cooled bolometer. Temperature dependent measurements were done for single-crystal CoO(100)/MgO(100) in the range from 100 to 300 cm^{-1} using the liquid-helium cryostat in the temperature range from 5 to 200 K.

The low tempereture optical microscopy and Raman studies were carried out by using a home-made micro-Raman spectrometer based on a standard Olympus microscope, equipped with single grating Andor Shamrock 303i spectrometer (focal length 303 mm, grating 600 lines/mm with a resolution of about 10 cm^{-1}) and TE cooled Andor Newton EMCCD camera. The Nd–YAG 532 nm laser excitation was used with intensity about 5 mW on the illuminated volume. A 50x objective was used, so that sampling volume was a cylinder with diameter 1.5 μm and depth about 14 μm. To carry out the low temperature measurements, a special Utreks-type cold finger helium cryostat was designed.

3. Results and discussion

The far-IR spectra for single-cristal CoO are shown in Fig. 1. The two AFMR bands at 221 and 249 cm^{-1} were relianly measured below 180 K and are in good agreement with previous work [4]. However, such bands were not observed in diluted samples $Co_cMg_{1-c}O$ for $c \leq 0.8$ down

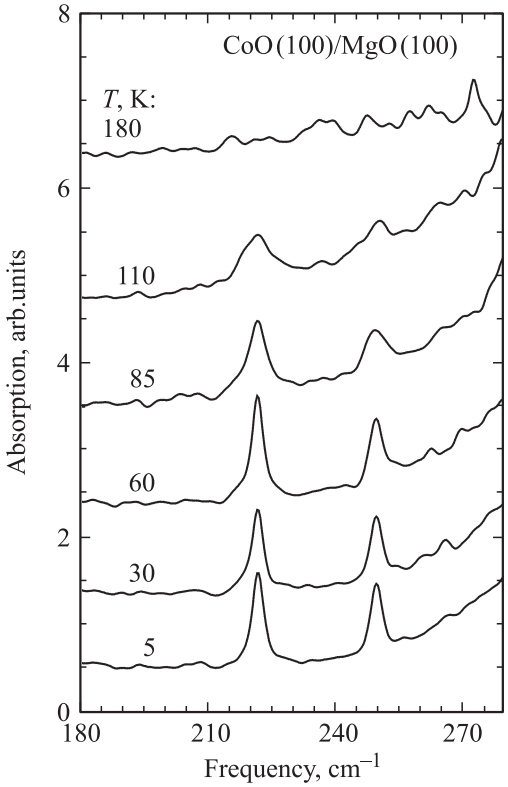

Figure 1. Far-IR optical absorption spectra in single-crystal CoO(100)/MgO(100). Two AFMR bands at 221 and 249 cm^{-1} are well visible below 180 K.

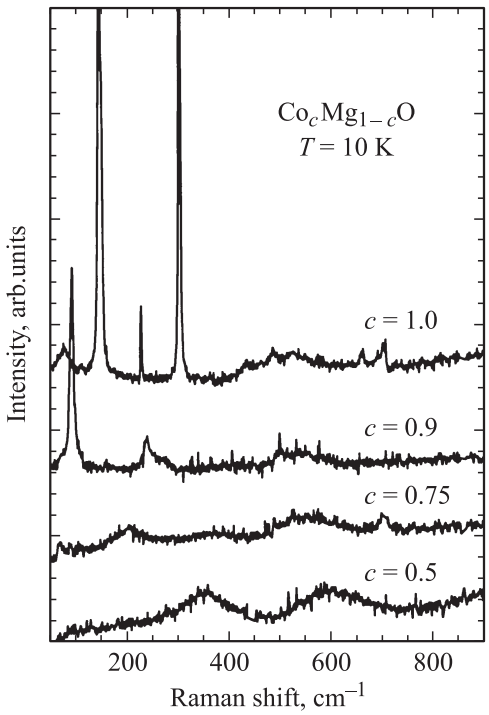

Figure 2. Raman spectra in $Co_cMg_{1-c}O$ solid solutions at $T = 10$ K. Two sharp peaks due to magnon excitations are well visible for $c = 1.0$ and 0.9.

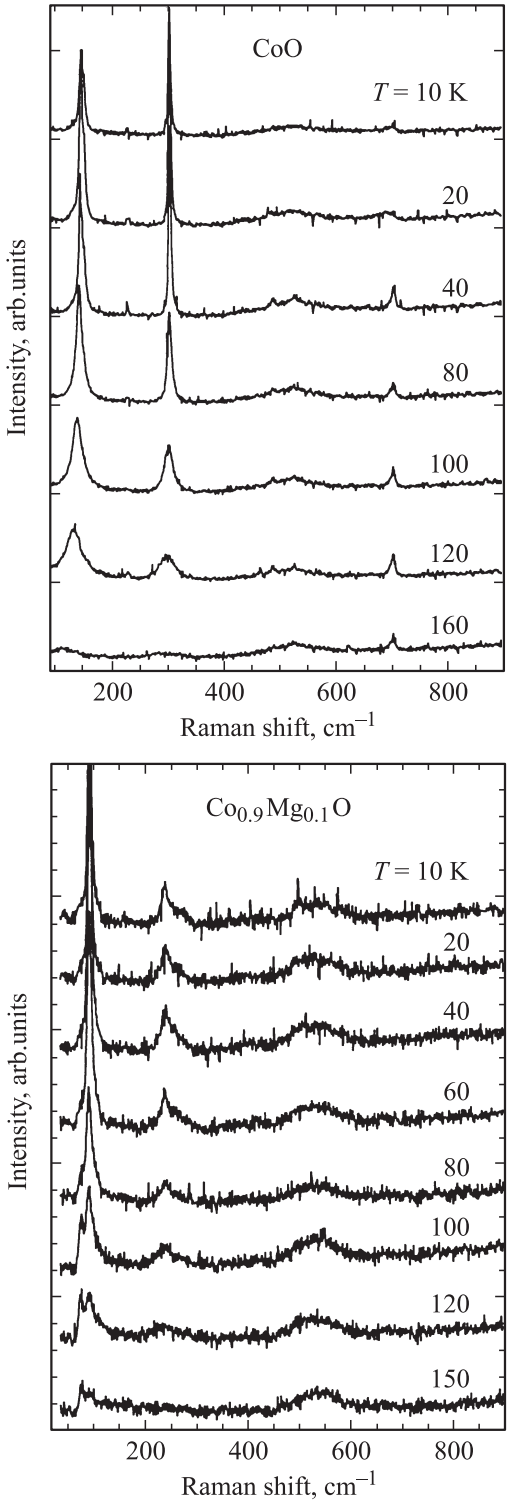

Figure 3. Temperature dependence of the Raman scattering in CoO and $Co_{0.9}Mg_{0.1}O$ solid solutions. Small peak at 700 cm^{-1} for CoO is due to an admixture of Co_3O_4 phase.

to 6 K, suggesting that the presence of defects, magnesium ions, destroys the long range magnetic ordering probed by AFMR, already at small dilution.

Composition dependence of Raman scattering in $Co_cMg_{1-c}O$ solid solutions at $T = 10$ K is shown in Fig. 2.

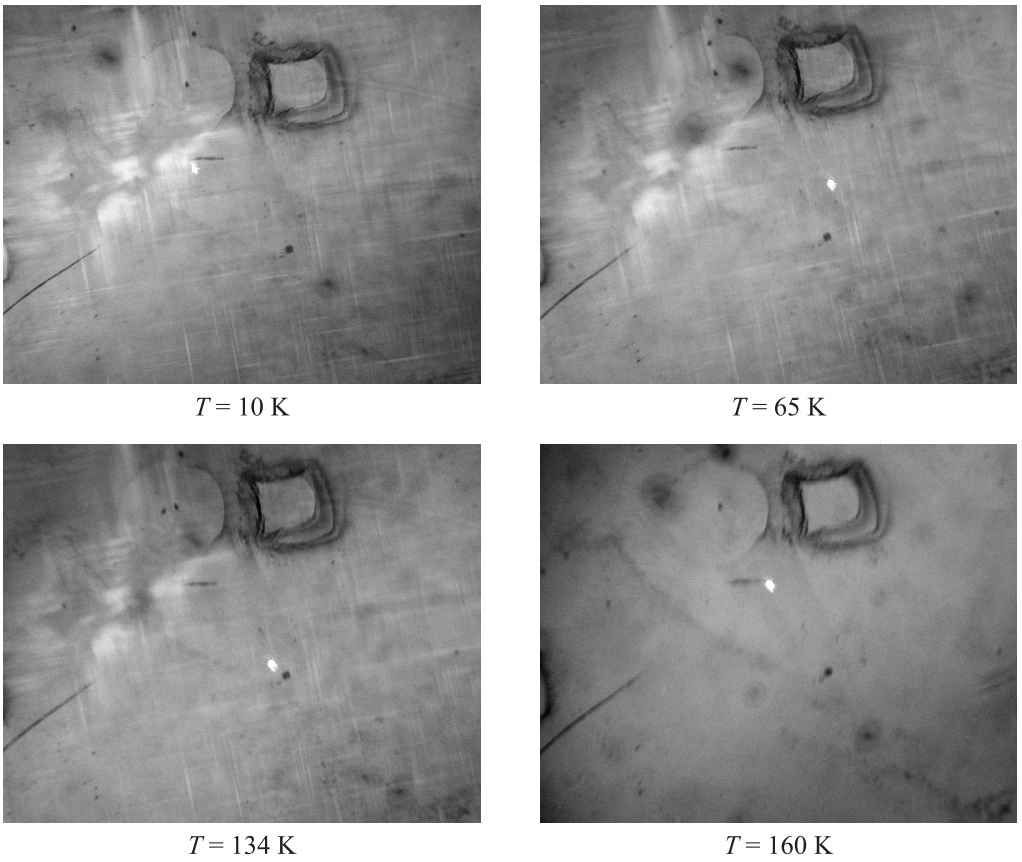

Figure 4. Twin domain structure of single-crystal $Co_{0.9}Mg_{0.1}O$ observed in polarized light through the optical microscope (50× objective). Image size is about $150 \times 80\,\mu$m.

Three sharp peaks due to the Brillouin zone center ($k = 0$) magnon excitations at 145, 229 and 305 cm^{-1} are well visible in pure CoO ($c = 1$), two peaks at 94 and 238 cm^{-1} remains for $c = 0.9$, but no peaks can be observed upon further dilution. Note that the results for pure CoO are in agreement with previous studies [5,6]. The broad band at 400–600 cm^{-1} is atributed to first-order Raman scattering by longitudinal phonons in the Brillouin zone center [7] and is visible for $c = 1.0$ and 0.9. For $c = 0.75$, another band grows up at 300–450 cm^{-1} and the former one begins to shift to higher frequencies. Finally, two separate bands at 250–450 and 500–700 cm^{-1} are observed for $c = 0.5$. They can be attributed to transverse and longitudinal phonons in the Brillouin zone center, respectively [7]. The variation of phonon bands positions occurs due to the change of the solid solution lattice parameter, which is larger in pure CoO ($a = 4.2615$ Å) than in MgO ($a = 4.2113$ Å) [1,8]. The pronounced compositional desorder at $c = 0.5$ is responsible for some increase of the Raman bands intensity.

Temperature dependence of the Raman scattering in CoO and $Co_{0.9}Mg_{0.1}O$ solid solutions is shown in Fig. 3. The magnon related bands decrease gradually upon temperature grow and disappear completely at about 160 K for $c = 1.0$ and at 140 K for $c = 0.9$. At the same time, the phonon related band at 400–600 cm^{-1} remains nearly unchanged. One should note that the first magnon peak, located at 92 cm^{-1} below 80 K, becomes splitted into peaks, located

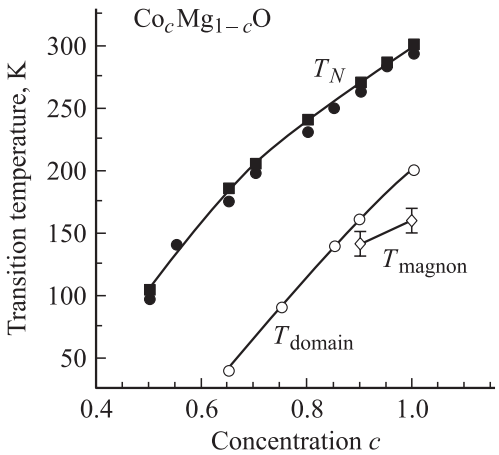

Figure 5. Magnenit phase diagram for $Co_cMg_{1-c}O$ solid solutions: the Néel temperature (T_N) according to the magnetic neutron diffraction [1] (solid squares) and magnetic susceptobility measurements [2] (solid circles); the temperature (T_{domain}) below which the structure exists (open circles); the temperature (T_{magnon}) below which the magnetic excitations are observed in Raman scattering and far-IR optical absorption (open diamonds).

at 75 and 91 cm^{-1} above 80 K, for $c = 0.9$, while it only broadens for $c = 1.0$. The origin of the splitting is not clear.

Antiferromagnetic domain structure was observed in single-crystal $Co_{0.9}Mg_{0.1}O$ using polarized light in the temperature range up to about 160 K (Fig. 4). The twin domains have widths of the order of a $0.5-2\,\mu$m and extend over tenths of μm. One can see that the presence of large defects at the surface of the sample do not influence the domain structure. This suggests that the observed domain pattern reflects the bulk domain structure.

In Fig. 5, the temperature dependence of the magnetic ordering in $Co_cMg_{1-c}O$ solid solutions is compared for several experimental techniques. One can see that the region of magnetic ordering, determined from the domain structure, Raman scattering and AFMR, exists well below the Néel temperature (T_N), estimated from neutron diffraction [1] and magnetic susceptibility [2] measurements. This fact can be explained by different magnetic interaction correlation lengths for these experimental techniques.

4. Summary and conclusions

We have studied the influence of dilution by magnesium ions on the magnetic ordering single-crystal $Co_cMg_{1-c}O$ solid solutions. It was observed that the twin domain structure and the contribution from magnetic excitations to Raman scattering and AFMR disappear well below the Néel temperature, determined by neutron diffraction and magnetic susceptibility measurements.

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