PROCEEDINGS OF SPIE
Optical Materials and Applications, ed. A. Rosental (6-9 July 2004, Tartu, Estonia)

Influence of radiation defects on exciton-magnon interactions in nickel oxide

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ABSTRACT

Influence of radiation defects on the optical absorption spectrum of nickel oxide (NiO) was studied at the temperature 6 K in the near infra-red energy range 7750-8300 cm^{-1}, corresponding to the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ at nickel sites. NiO single-crystals, grown by the method of chemical transport reactions on MgO(100) substrates, were irradiated by the neutron fluences up to $5x10^{18}$ cm^{-2}. Two sharp lines were observed at the low-energy side of the band: the peak at 7805 cm^{-1} is assigned to the pure exciton transition, whereas the peak at 7845 cm^{-1} to the exciton-magnon excitation, which occurs at the Brillouin zone-centre (BZC). An increase of the defects concentration at higher fluences results in a lowering of the magnon satellite peak intensity. The long-wavelength BZC magnon absorption is sensitive to the long-range magnetic ordering, which becomes destroyed in the presence of radiation defects. Therefore, the observed decrease of the peak intensity is attributed to a decrease of the spin-spin correlation length due to inhomogenious broadening.

Keywords: NiO, magnetic-dipole transition, radiation defects, magnons

1. INTRODUCTION

The electronic and magnetic structure of nickel oxide (NiO) is a subject of continuous interest during many years [1]. NiO is a type-II easy-plane antiferromagnet with the Néel temperature T_N = 523 K [2]. In the paramagnetic phase, it has a rocksalt-type crystal structure, whereas a week cubic-to-rhombohedral distortion occurs below T_N in the antiferromagnetic phase [3]. The antiferromagnetic structure of NiO is characterized by dominating superexchange interactions ($J_{NNN} \approx 150$ cm^{-1}) between the next-nearest-neighbours (NNN), connected by 180º Ni^{2+}-O^{2-}-Ni^{2+} linear atom chains. Much weaker superexchange coupling ($|J_{NN}| \approx 11$ cm^{-1}) occurs between the nearest-neighbours (NN), connected by 90º Ni^{2+}-O^{2-}-Ni^{2+} paths [4-6]. The exchange interactions in NiO not only influence its magnetic properties but also appear in optical absorption [7-11], photoluminescence [12], and Raman scattering [4,6,13-17] spectra.

The magnetic properties of nickel oxide can be strongly modified by the presence of impurity atoms and radiation defects [18]. For example, substitution of a part of nickel ions by magnesium ions results in a continuous series of $Ni_cMg_{1-c}O$ solid solutions, having a rich magnetic phase diagram [3,19]. At T = 0 K, it consists of four regions: (1) a homogeneous antiferromagnet ($0.63 \le c \le 1$), (2) a cluster antiferromagnet ($0.4 \le c < 0.63$), (3) spin-glass type ($0.25 \le c < 0.4$), and (4) a paramagnet ($c \le 0.2$). A number of other mixed systems as $Li_xNi_{1-x}O$ [20], $Co_xNi_{1-x}O$ [21,22] and $Fe_xNi_{1-x}O$ [23] were also studied. The influence of neutron irradiation on optical absorption spectra in NiO and $Ni_cMg_{1-c}O$ solid solutions was studied in [18]: it was found that irradiation increases mainly the intensity of spin-forbidden optical transitions.

In the present study we will concentrate on the optical absorption. The absorption bands observed in nickel oxide are related to parity-forbidden *d–d* transitions and can be labelled using the energy level diagram of a free nickel ion $Ni^{2+}(3d^8)$ in a cubic crystal field. Three transitions from the $^3A_{2g}(F)$ ground state to the $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$

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excited states are spin-allowed (ΔS=0), but the others are spin-forbidden. The bands in UV and visible spectrum ranges are the electric-dipole in nature, whereas the near-IR band at 8800 cm^{-1} corresponds to the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ [18]. We have found previously [7,9-11] that the last band contains at low temperatures two zero-phonon lines, located at about 7805 cm^{-1} and 7845 cm^{-1}, due to the pure exciton and exciton–one-magnon excitations, respectively. The intensity of the exciton–one-magnon line varies strongly both with temperature [10,11] and composition [9,11], due to homogeneous and inhomogeneous broadening, respectively.

In this work, we discuss for the first time an influence of the radiation defects, produced by neutrons, on the exciton–one-magnon zero-phonon transition within the magnetic-dipole $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ band in NiO.

2. EXPERIMENTAL

Single-crystal NiO(100) were grown epitaxially on freshly cutted and polished single-crystal MgO(100) substrates by chemical transport reactions method (the "sandwich" technique) using HCl gas [24]. Thus obtained NiO crystals have green colour and retain orientation of the MgO substrate. Several samples of NiO were irradiated at the Salaspils (Latvia) nuclear reactor by the fast neutrons with the energy >0.1 MeV and fluences $1.8x10^{18}$ and $5x10^{18}$ cm^{-2}. The cadmium filter was used to eliminate thermal neutrons. The irradiation was performed by placing the samples into the water channel, so that the samples temperature during irradiation was maintained below 400 K. Optical absorption spectra were recorded using the split-beam Jasco spectrophotometer (Model V-570) with the tungsten iodine lamp used as a source. PbS photoconductive cell was used as a detector. A liquid helium cryostat was used to control the temperature of the samples down to 5 K with an accuracy ±1 K.

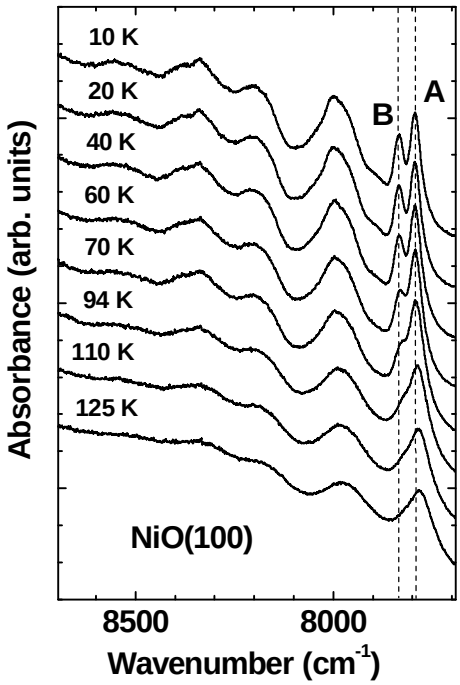

Figure 1: Temperature dependence of the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ absorption band in NiO(100) single-crystal. Peak A corresponds to pure exciton absorption, whereas peak B to the exciton–one-magnon excitation. The fine structure above 7900 cm^{-1} is due to the exciton–phonon excitations.

3. RESULTS AND DISCUSSION

The magnetic-dipole band $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ in NiO consists at T=10 K of two sharp zero-phonon lines (peaks A and B in Fig. 1), phonon satellite peaks and a broad sideband [7,10]. The peak A at ~7805 cm^{-1} is attributed to the pure exciton transition, whereas the peak B at ~7845 cm^{-1} to the simultaneous exciton–one-magnon excitation [7,10]. Here the one-magnon excitation occurs at the Brillouin zone-centre, and its energy can be obtained as the difference between peaks A and B [10]. Upon increasing temperature or creation of defects under neutron fluence, the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ band experiences homogeneous and inhomogeneous broadening, which affects the intensity and the position of the two zero-phonon peaks and of the phonon sideband [25].

Temperature dependence of the one-magnon sideband in NiO is shown in Fig. 1. Note that the peak B disappears above 110 K that is well below the Néel temperature T_N =523 K. The separation between two peaks A and B remains constant at all measured temperatures and equals to about 41 cm^{-1}. This value is in agreement with that obtained previously by far-infrared antiferromagnetic resonance (AFMR) [26,27] and by Raman scattering [14-17]. A small shift of both (A and B) peaks as well as of the band maximum to smaller energies, observed upon temperature increase, is attributed to the change of the crystal field strength due to the thermal lattice expansion [18].

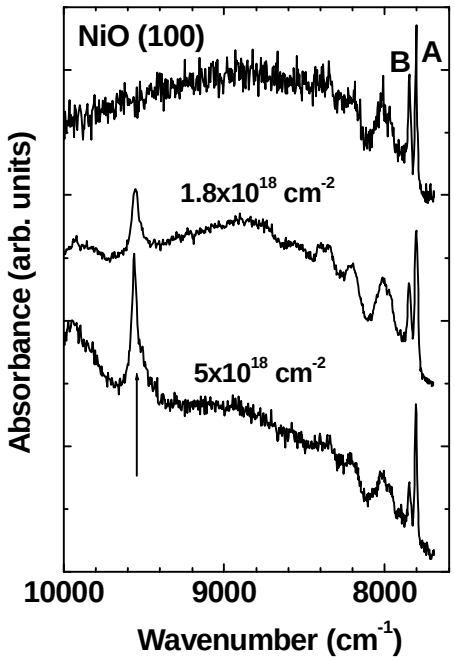

Figure 2: The $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ absorption band in NiO(100) single-crystals, measured at the temperature T = 6 K. The two lower curves correspond to samples, irradiated by the neutron fluences $1.8x10^{18}$ and $5x10^{18}$ cm^{-2}. They contain a sharp peak at ~9550 cm^{-1}, associated with the radiation defects Fe^{2+} in MgO substrate. Peak A corresponds to pure exciton absorption, whereas peak B to the exciton–one-magnon excitation. The fine structure above 7900 cm^{-1} is due to the exciton–phonon excitations.

Previous investigations [18] of the influence of neutron irradiation on optical absorption spectra of pure nickel oxide and $Ni_cMg_{1-c}O$ solid solutions have shown that the irradiation increases intensity of spin-forbidden transitions and does not affect the intensity of spin-allowed transitions. An increase of the spin-forbidden transitions intensity occurs due to the exchange interaction between 3d electrons of nickel ion and the electron, localized at a defect site [18,28]. Such interaction should produce opposite effect, i.e. results in a decrease of intensity for the magnon assisted absorption, since the presence of radiation defects will destroy periodic magnetic ordering. Previously we have found that a substitutional modification of the magnetic sublattice by an admixture of less than 10% of magnesium ions to nickel oxide leads to a strong damping of the peak B intensity already at T = 6 K [3,19]. As one can see in Fig. 2, irradiation of nickel oxide with neutrons leads to a lowering of the peak B intensity, which decreases with an increase of the neutron fluence due to inhomogeneous broadening produced by the presence of radiation defects.

Besides, a sharp peak at 9550 cm^{-1} and a fine structure above it are observed for our samples after irradiation. Their intensity increases with the neutron fluence variation from $1.8x10^{18}$ cm^{-2} to $5x10^{18}$ cm^{-2}. We associate the peak at 9550 cm^{-1} and the fine structure above it with the transition $^5T_{2g} \rightarrow {}^5E_g$ in the radiation induced defects Fe^{2+} present in MgO substrate [29,30].

4. CONCLUSIONS

Influence of temperature and irradiation by neutrons on the optical absorption spectrum of nickel oxide was studied in the near infra-red energy range 7750-8300 cm^{-1}. This interval corresponds to the magnetic-dipole transition $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ at Ni^{2+} sites. Two sharp lines were observed at the low-energy side of the band: the peak at 7805 cm^{-1} is assigned to the pure exciton transition, whereas the peak at 7845 cm^{-1} to the exciton-magnon excitation (magnon sideband), which occurs at the Brillouin zone-centre (BZC). An increase of temperature or of the defects concentration at high neutron fluences results in a lowering of the magnon satellite peak intensity. The effect of temperature leads to a homogenious broadening of the magnon sideband. At the same time, a decrease of the magnon sideband intensity upon irradiation with neutrons is attributed to a distruction of the long-range magnetic ordering due to inhomogenious broadening.

ACKNOWLEDGMENTS

This work was partially supported by grants of the Latvian Government (No. 01.0806 and 01.0821) and the Estonian Science Foundation (No. 3453).

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