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Behavior of one-magnon frequency in antiferromagnetic $Ni_cMg_{1-c}O$ solid solutions

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The one-magnon scattering was studied in antiferromagnetic $Ni_cMg_{1-c}O$ solid solutions. We observed unpredicted behavior of both temperature and composition dependences of one-magnon excitation energies. First, the abrupt change of the one-magnon frequency by 7–8 cm^{-1} occurs between $c=0.98$ and $c=0.9$ in the limit of $T\rightarrow 0$ K. Second, upon increasing temperature, the one-magnon energy for highly diluted nickel oxide vanishes significantly below the Néel temperature.

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I. INTRODUCTION

The $Ni_cMg_{1-c}O$ system forms a continuous series of solid solutions with a rock-salt crystal structure,[1,2] due to a small difference (about 0.02 Å) of the ionic radii of Ni^{2+} and Mg^{2+} ions, allowing them to substitute each other. The lattice constant of $Ni_cMg_{1-c}O$ solid solutions varies[3] from 4.177 Å in pure NiO ($c=1$) to 4.212 Å in pure MgO ($c=0$) close to the linear dependence, predicted by the Vegard's law.[2] More precisely, the lattice constant values lie slightly below (up to 0.002 Å the Vegard's model prediction,[3] due to the off-center displacement of the nickel ions,[4] caused by the 90° superexchange interactions[6,7] ($J_{NN}\simeq 11$ cm^{-1} in Ref. 5) between two nearest-neighbor (NN) Ni^{2+} ions via an oxygen ion. It is noteworthy that such an exchange-coupling of NN Ni^{2+} ions leads to a formation at $0.01<c<0.2$ of isolated Ni^{2+}-Ni^{2+} pairs, observable in photoluminescence spectra.[8]

The magnetic properties of the $Ni_cMg_{1-c}O$ system vary strongly with the composition from antiferromagneticlike behavior, for pure NiO, to diamagneticlike behavior for pure MgO.[1,2] For intermediate compositions with $c>0.3$, the paramagnetic-to-antiferromagnetic phase transition occurs upon cooling.[1,2] Thus, the simplicity of the crystal structure and the ease of preparation make the $Ni_cMg_{1-c}O$ solid solutions an ideal system to study the physics of diluted antiferromagnets and, in particular, the magnon excitations.

In this paper, we present the composition ($0.5<c<1.0$) and temperature ($10<T<400$ K) dependence of the one-magnon Raman scattering in the $Ni_cMg_{1-c}O$ system. Both dependences show unpredicted behaviors for diluted compositions ($c<1$).

Pure NiO is a type II easy-plane antiferromagnet with the Néel temperature $T_N=523$ K.[9] Below T_N, the spins of the Ni^{2+} ions in NiO are ordered ferromagnetically in $\{111\}$ planes, where they lie along the $\langle 11\overline{2}\rangle$ axes.[5,10] The antiferromagnetic structure of NiO is determined by dominating superexchange interactions ($J_{NNN}\simeq 150$ cm^{-1} in Refs. 5 and 11) between next nearest-neighbors (NNN) in the linear atom chains Ni^{2+}-O^{2-}-Ni^{2+}. The magnons-dispersion curves in NiO were determined by inelastic neutron scattering in Ref. 5. Near the Brillouin zone center (BZC), two magnon modes were observed, which correspond to antiferromagnetic resonance (AFMR) out-of-plane and in-plane modes.[5] The out-of-plane AFMR mode was detected at 36.6 cm^{-1},[5] and it was also found in far-infrared absorption spectrum of NiO in Refs. 12 and 13. The in-plane AFMR mode was observed at ~8 cm^{-1} in Ref. 5.

Magnon excitations in pure NiO were successfully probed in the past by Raman spectroscopy. In particular, the one-magnon,[14–17] two-magnons[11,14,18–20] and four-magnons[19] scattering was detected.

Temperature-dependent measurements of the one-magnon scattering in black (oxygen-deficient) NiO evidenced a doublet structure (37.6 and 43.8 cm^{-1} at 10 K), which melts into one broad line at room temperature: it was attributed to surface and bulk magnon modes, respectively.[14] On the other hand, more recent measurements carried out on green NiO did not show clear evidence of the doublet peak shape.[16] Note that the observed temperature dependence of the one-magnon scattering in pure NiO is in good agreement with theoretical predictions for the BZC magnon frequency ω_{1M}.[21,22]

The two-magnon scattering in NiO occurs, in the limit of $T\rightarrow 0$ K, at $\omega_{2M}\simeq 1550$ cm^{-1} and is associated with the Brillouin zone-boundary (BZB) magnons excitation. This scattering has a relatively higher intensity when compared to other magnon excitations, since the magnons density is strongly peaked at the BZB.[5] Temperature dependence of the two-magnon scattering was studied in Ref. 18 and shows expected behavior.[23] The four-magnons scattering in pure NiO is very weak and was observed only in Ref. 19.

Pressure dependence of the one-magnon[17] and two-magnon[11] scattering in NiO was also studied and was explained by the variation of the dominating NNN exchange energy J_{NNN} as a function of lattice constant.

Only two works[20,24] exist to our knowledge dealing with the magnetic excitations in diluted nickel oxide. In Ref. 24, two-magnon Raman scattering was measured in calcium-doped NiO with calcium content up to 6 mol %. It was found that upon dilution, the position and shape of the two-magnon band follow the expected behavior.[21,22]

In our previous work on $Ni_cMg_{1-c}O$ solid solutions,[20] the dependence of the two-magnon band on the composition and temperature was studied by Raman spectroscopy in a wide range of compositions $(0.3 < c < 1)$ and temperatures $(10-300\ K)$. The observed variations of the two-magnon scattering[20] are consistent with the magnetic phase diagram[1] of the $Ni_cMg_{1-c}O$ system.

In the present paper, we extend our studies to the case of long-wavelength one-magnon scattering, which is more sensitive to the destruction of the long-range magnetic order upon dilution than the short-wavelength two-magnon scattering does.

II. EXPERIMENT

The samples used in our experiments were both polycrystalline and single crystal. Polycrystalline pure NiO and solid solutions $Ni_cMg_{1-c}O$ with $c=0.9$ and $c=0.5$ were prepared using ceramic technology from the appropriate amounts of aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ 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 $T_{an}=1200\ °C$ in air and then quickly cooled down to room temperature. Single-crystal solid solutions with $c=0.99$, 0.98, 0.80, and 0.60 were grown epitaxially from polycrystalline $Ni_cMg_{1-c}O$ solid solutions of the same composition on freshly cut and polished single-crystal MgO(100) substrates by the method of chemical transport reactions using HCl gas as the transport medium.[25] The single crystals had a size of about $6 \times 6 \times 1\ mm^3$.

All the obtained samples had a green color. The chemical composition of solid solutions was controlled by instrumental neutron-activated analysis.[26] It was confirmed that the content of nickel in the samples was in agreement with the stoichiometric one within ±0.005–0.01 depending on the composition. For high nickel content in $Ni_cMg_{1-c}O$ solid solutions with $c=0.99, 0.98$, the estimated accuracy is ±0.005, whereas it decreases to ±0.01 going to lower nickel concentrations $(c=0.5)$. Our previous x-ray absorption spectroscopy studies indicate also that the number of nickel and magnesium ions in the second shell of nickel ions varies in agreement with the uniform distribution model.[4]

Temperature-dependent measurements were carried out from 10 to 400 K using standard macro-Raman apparatus, with a right-angle scattering geometry. The Raman spectra were excited by the 5145-Å line of an argon laser, with a nominal power of 100 mW at the cryostat window. The samples were mounted in a liquid helium flux cryostat, and the temperature was controlled within ±2 K. The scattered radiation was focused at the entrance slit of a one-meter focal length double monochromator (Jobin-Yvon, model Ramanor HG2-S), mounting concave holographic gratings (2000 grooves/mm). The experimental resolution was of the order of $3\ cm^{-1}$. The filtered radiation was detected by a cooled (−35 °C) photomultiplier tube (RCA, model C31034A-02), operated in photon-counting mode. The signal was stored into a multichannel analyzer and then sent to a microcomputer for the analysis. The Raman spectra were recorded at $0.5\ cm^{-1}$ spectral steps from −80 to $90\ cm^{-1}$, thus including both anti-Stokes (magnon annihilation) and Stokes (magnon creation) parts. Note that all Raman experiments were performed in zero magnetic-field conditions.

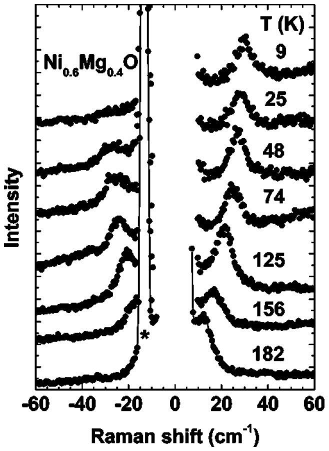

FIG. 1. Temperature dependence of the one-magnon scattering in $Ni_{0.6}Mg_{0.4}O$ solid solution in the anti-Stokes and Stokes Raman spectra. The asterisk indicates the position of a plasma line from argon laser.

III. RESULTS AND DISCUSSION

Representative experimental results of the one-magnon scattering in $Ni_cMg_{1-c}O$ system are shown in Figs. 1 and 2 for two compositions $c=0.6$ and $c=0.8$.

Figure 1 clearly indicates that one-magnon excitation, corresponding to the out-of-plane AFMR mode, can be well observed in both anti-Stokes and Stokes parts of the Raman spectrum. This allows for more precise determination of the

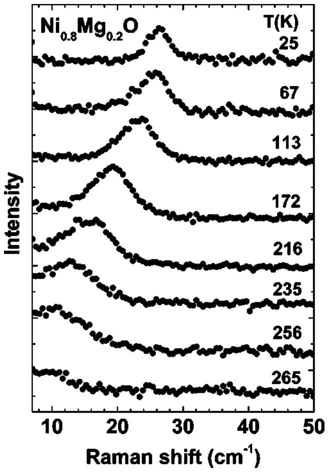

FIG. 2. Temperature dependence of the one-magnon scattering (the Stokes part) in $Ni_{0.8}Mg_{0.2}O$ solid solution.

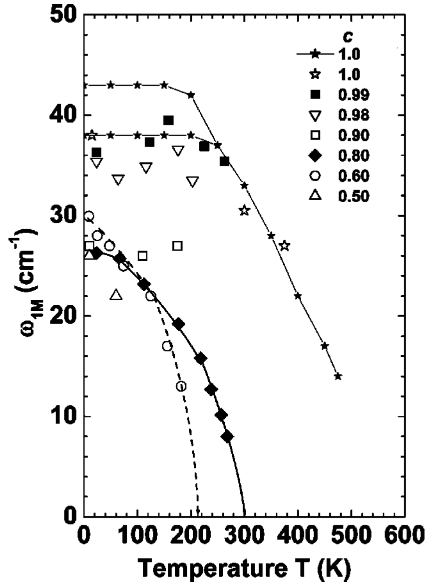

FIG. 3. Temperature dependence of the one-magnon frequency values in NiO and $Ni_cMg_{1-c}O$ solid solutions. The data for pure NiO from Ref. 16 are schematically shown for comparison by interconnected stars (see text for details).

one-magnon frequency ω_{1M}. Note that the in-plane mode, expected[5,21] at ~8 cm^{-1}, cannot be observed in our experiment due to an overlap with the elastic scattering of laser light. For $c=0.6$, the one-magnon frequency, extrapolated to $T=0$ K, is about 29 ± 1.5 cm^{-1}. Upon increasing temperature, the magnon frequency decreases and the peak broadens. No magnon contribution is detected for $c=0.6$ above about 190 K due to strong overlap between the magnon peak and the too-much intense tail of the elastically scattered laser light. The extrapolation of the temperature dependence of the one-magnon frequency to $\omega_{1M}=0$ (Fig. 3) gives the critical temperature T_C of about 210 K, which is much smaller than the Néel temperature $T_N(c=0.6)\simeq 310$ K.[1] Note that this difference is significantly beyond the error of the T_C determination, estimated to be about ±30 K at maximum.

Figure 2 shows the temperature behavior of the one-magnon Stokes scattering in $Ni_{0.8}Mg_{0.2}O$. Here the magnon contribution is detectable up to about 270 K, and the one-magnon frequency extrapolated to $T=0$ K is about 26 ± 1 cm^{-1}. The magnon frequency decreases and the peak progressively broadens upon temperature increase. The extrapolation of the temperature dependence of the one-magnon frequency to $\omega_{1M}=0$ (Fig. 3) gives the critical temperature T_C of about 300 K, that is, as for $c=0.6$, remarkably lower than the Néel temperature $T_N(c=0.8)\simeq 420$ K.[1]

Temperature dependences of the one-magnon frequency for all the measured compositions are shown in Fig. 3. Here we present also for comparison the data for pure NiO from Ref. 16. Note that due to a double-peak model utilized in Ref. 16 to describe the magnon peak at low temperatures, there are two magnon frequencies below 240 K. Our results for pure NiO did not reveal any reliable splitting of the one-magnon peak shape, therefore only one magnon frequency was obtained, which overlaps well with the lower frequency magnon values of Ref. 16. Note that our temperature dependence of the one-magnon frequency in NiO is in close agreement with the theoretical prediction from Ref. 22, based on the exchange and single-ion anisotropy parameters determined by the neutron-scattering experiments.[5]

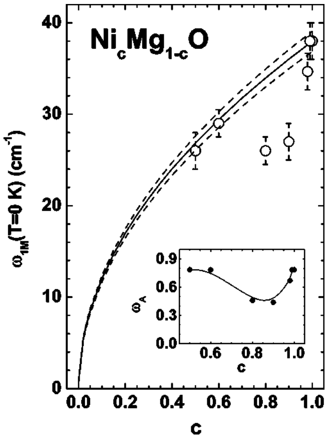

FIG. 4. Composition dependence of the one-magnon frequency in the limit of $T\rightarrow 0$ K in NiO and $Ni_cMg_{1-c}O$ solid solutions. The solid line is the theoretical prediction from equation (Ref. 27) $\omega_{1M}=(2\omega_E\omega_A+\omega_A^2)^{1/2}$. The two dashed lines indicate the deviation of ω_{1M} due to uncertainty in ω_A and J_{NNN} (Ref. 5). The inset figure shows dependence of the single-ion anisotropy frequency ω_A versus the sample composition, determined by fitting the previous expression to each experimental point separately. The solid line in the inset is only a guide for the eyes.

The dilution of nickel oxide with magnesium ions results into a decrease of the one-magnon frequency. However, as one can see in Fig. 3, this decrease is not uniform. In the limit of $T\rightarrow 0$ K, the one-magnon frequency changes only slightly for the compositions $0.98\leqslant c\leqslant 1.0$, for smaller values of c an abrupt lowering of the ω_{1M} value is observed for $c=0.90$, but no significant variation of ω_{1M} is found for $0.5<c<0.9$. In fact, the one-magnon frequency at $T\rightarrow 0$ K for the samples with $c=0.9$, 0.8, 0.6, and 0.5 falls within the interval 27 ± 3 cm^{-1} (Fig. 3).

The one-magnon frequency in zero magnetic field is given by $\omega_{1M}=(2\omega_E\omega_A+\omega_A^2)^{1/2}$,[27] where $\omega_E=zSJ_{NNN}$ is the exchange frequency, ω_A is the single-ion out-of-plane anisotropy frequency, z is the number of the magnetic neighbors, and S is the spin. In the case of solid solutions, the conventional approach is to substitute z with zc,[28] so that $\omega_E=zcSJ_{NNN}$. It was used previously to explain succesfully the composition dependence of the one-magnon Raman scattering for $Fe_{1x}Zn_xF_2$ solid solutions in Ref. 28. The result of the calculation for $Ni_cMg_{1-c}O$ is shown in Fig. 4. Here we used $S=1$, $z=6$, $J_{NNN}=153\pm3$ cm^{-1}, and $\omega_A=0.785\pm0.03$ cm^{-1} (the two latter values are from Table IV of Ref. 5). As one can see, such predicted dependence of the one-magnon frequency on the composition (solid line in Fig. 4) deviates significantly from our experimental observations.

In the above-mentioned expression for ω_{1M}, the two parameters, J_{NNN} and ω_A, may differ from their values in pure NiO upon dilution by magnesium ions.

An estimate for the variation of the exchange constant J_{NNN} in $Ni_cMg_{1-c}O$ can be obtained by combining the results of the pressure dependent magnetic Raman studies[11,17] with structural information provided by x-ray diffraction (XRD) (Ref. 3) and x-ray absorption spectroscopy (XAS).[4,29] Pressure dependence of the two-magnon Raman scattering[11] shows that a decrease of the lattice parameter in pure NiO from 4.18 Å at ambient pressure to about 4.02 Å at 30 GPa results in a linear increase of the superexchange constant J_{NNN} from 153 to 220 cm^{-1}. The pressure effect on the one-magnon Raman scattering, measured in Ref. 17 up to 20.3 GPa, leads to the same results. Therefore, one could expect that a change of the lattice parameter in $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ solid solutions can cause the change of J_{NNN}.

Precise XRD studies[3] indicate that the lattice constant in $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ solid solutions increases by only 0.015 Å from pure NiO to $\mathrm{Ni}_{0.5}\mathrm{Mg}_{0.5}\mathrm{O}$ that could cause a decrease of J_{NNN} by about 6 cm^{-1}. However, a nearly constant intensity of the pre-edge peak, observed by XAS (Ref. 29) at the Ni-K edge, suggests that J_{NNN} remains constant upon dilution. Therefore, an abrupt change of the one-magnon frequency in Fig. 4 seems to be not determined by J_{NNN}, but should be attributed to the change of the single-ion anisotropy energy ω_A. The latter can be estimated (see the inset in Fig. 4) from the obtained variation of the one-magnon frequency by fitting the above expression for $\omega_{1\mathrm{M}}$ to each experimental point separately and assuming that $J_{\mathrm{NNN}}=\mathrm{const}$. Thus obtained variation of ω_A with composition is unclear and could be attributed to the change of the local environment around nickel ions upon dilution.

Another interesting phenomenon, observed in $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ solid solutions, is related to the dependence of the critical temperature T_C, at which $\omega_{1\mathrm{M}}(T_C)\rightarrow 0$, on the composition. In pure NiO, T_C for the one-magnon frequency is close to the Néel temperature T_N (Fig. 3). However, our results clearly indicate that in solid solutions with $c=0.6$ and $c=0.8$, where the number of experimental points $\omega_{1\mathrm{M}}(T)$ allows for a reliable extrapolation to T_C with an uncertainty of the order of 10 K, T_C value given by the above extrapolation is about 100 K lower than T_N, obtained by neutron diffraction and magnetic susceptibility.[1,2] Close behavior for one-magnon excitation was observed recently for joint exciton-one-magnon transition in the region of the magnetic-dipole $^3A_{2g}(G)\rightarrow {}^3T_{2g}(F)$ optical absorption band in $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ single crystals.[30] However, in the latter case, the intensity of the one-magnon-assisted transition decreases rapidly with increasing magnesium ion concentration and/or temperature: it vanishes altogether at $T=6$ K for $c<0.95$ and at $T=130$ K for $c\geqslant 0.99$,[30] due to additional broadening of the exciton excitation. One should note also that in the case of $\mathrm{Fe}_{1-x}\mathrm{Zn}_x\mathrm{F}_2$ solid solution, the one-magnon Raman scattering was observed at least up to the Néel temperature.[28] Therefore, it can be concluded that the one-magnon scattering in $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ solid solutions is very sensitive to the destruction of the long-range magnetic ordering with increasing concentration of the diamagnetic magnesium impurity ions (static disorder).

IV. SUMMARY AND CONCLUSION

The one-magnon scattering was studied in antiferromagnetic $\mathrm{Ni}_c\mathrm{Mg}_{1-c}\mathrm{O}$ solid solutions. Note that the samples used in the present work were characterized and deeply investigated previously by several experimental techniques as neutron[1] and x-ray[3] diffraction, instrumental neutron-activated analysis,[26] optical absorption and luminescence,[8,30] Raman scattering,[20] and x-ray absoption spectroscopy.[4,29]

Two unexpected results were found for temperature and composition dependences of one-magnon excitation energies. We observed clearly an abrupt change of the one-magnon frequency by 7–8 cm^{-1} between $c=0.98$ and $c=0.9$ in the limit of $T\rightarrow 0$ K. Besides, we found that upon increasing temperature, the one-magnon energy for highly diluted nickel oxide vanishes significantly below the Néel temperature. While it is difficult to suggest any theoretical model that is able to explain the observed behavior, we belive that its origin comes from the destruction of the long-range magnetic ordering upon increasing concentration of magnesium ions. We would like to remember that no strange behavior was observed by us previously in two-magnon scattering from the same samples,[20] which depends on the short-range magnetic order

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