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Magnetic and Raman Scattering Studies on Intercalation Compounds Fe_xNbS_2

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Raman scattering spectra and magnetic susceptibility are measured in intercalation compounds Fe_xNbS_2 ($0.159 \leqq x \leqq 0.325$). A strong modification of Raman spectra is observed in a sample with x=0.239 (~ 0.25) which is accompanied by $2a \times 2a$ structural change and antiferromagnetic ordering. Some correlations between magnetic ordering (antiferromagnetic or spin glass) and structural change are also discussed for wide range of Fe contents x.

Keywords: Intercalation; Fe_xNbS_2; Superstructure; Raman scattering; Magnetic susceptibility; Magnetic interaction

INTRODUCTION

The interaction between host conduction electrons and the intercalated magnetic guests gives rise to new properties associated with a structural change as well as a magnetic ordering in transition-metal dichalcogenide intercalation compounds [1-8]. It was known in intercalation compounds Fe_xNbS_2 that the antiferromagnetic ordering in the $2a \times 2a$ superstructure appears at x=0.25 [1-4], and further the spin glass states occur in different Fe contents [5].

This paper presents experimental results of Raman scattering and magnetic susceptibility measurements in Fe_xNbS_2 ($0.159 \leqq x \leqq 0.325$). They show that the $2a \times 2a$ superstructure in x=0.239 (~ 0.25) is quite favorable to the appearance of an antiferromagnetic ordering than the other guest configurations

in $0.281 \leqq x \leqq 0.325$.

EXPERIMENTAL

The samples used were 2H-NbS_2 and single crystals of Fe_xNbS_2 ($0.159 \leqq x \leqq 0.325$) grown by a chemical vapor transport technique using iodine as a carrier agent. The Fe contents x are evaluated by EPMA. The electron diffraction patterns of the samples at characteristic contents x=0.239 and 0.325 show the $2a \times 2a$ and $\sqrt{3}a \times \sqrt{3}a$ superstructures, respectively.

Polarized and depolarized Raman scattering experiments at 300 K were carried out in backscattering geometry by using an excitation source 514.5 nm emission from an Ar^+ laser. The incident and scattered lights are parallel to the c-axis of the single crystal. Magnetic susceptibility measurements have been done by using a static-field mode of a SQUID magnetometer in the temperature range 5 to 300 K. The magnetic field is applied parallel (//) and perpendicular ($\perp$) to the c-axis of the stacked crystals; sample weights are 10-20 mg. These experiments are carried out by using samples picked up from the same batch, because the quality of crystal depends on synthetic conditions.

RESULTS AND DISCUSSION

Figure 1 shows the depolarized Raman spectra of the Fe_xNbS_2 crystals at 300 K. The Raman spectra from samples with lower contents x=0.159 and 0.199 exhibit three peaks at 150, 340 and 380 cm^{-1}. Referring to theoretical results for the host NbS_2 [9], they can be assigned to the two-TA phonons, E_{2g} phonon and A_{1g} phonon Raman lines, respectively. They are similar to those of 2H-NbS_2 [10]. This indicates that the intercalated Fe ions do not break the crystal symmetry and occupy randomly at the octahedral sites. At x=0.239, the Raman spectrum changes dramatically. The higher A_{1g} and E_{2g} optical phonon lines split into a few peaks and the scattering intensities of lower three lines below 200 cm^{-1} are enhanced strongly. In the range of $0.281 \leqq x \leqq 0.325$, the

observed optical phonon Raman spectra differ from those of x=0.239. Comparing the spectra of x=0.239 and those of $0.281 \leqq x \leqq 0.325$, we attribute the difference to the formations of the $2a \times 2a$ superstructure in x=0.239 and of the $\sqrt{3}a \times \sqrt{3}a$ superstructure in $0.281 \leqq x \leqq 0.325$.

It should be noted again that the strong enhancement and the change of the lower Raman lines in x=0.239 are very interesting in the context of charge density wave (CDW) instability. The softening of the acoustic phonon modes was observed by Raman scattering [11] which indicates the CDW instability associated with a strong d-electron and TA phonon coupling.

The phonon energies are plotted against the Fe contents x as shown in Fig. 2. Both energies of A_{1g} and E_{2g} modes increase about 10 and 40 cm^{-1}, respectively, when the x value increases from 0 to 0.325. The increase of phonon energies is understood by the hardening of the spring constant due to charge transfer from intercalated Fe ions to the host S layer.

Figure 3 shows the temperature dependence of the magnetic susceptibilities $\chi_{//}$ and $\chi_{\perp}$ for the sample of x=0.245. Both $\chi_{//}$ and $\chi_{\perp}$ attain a

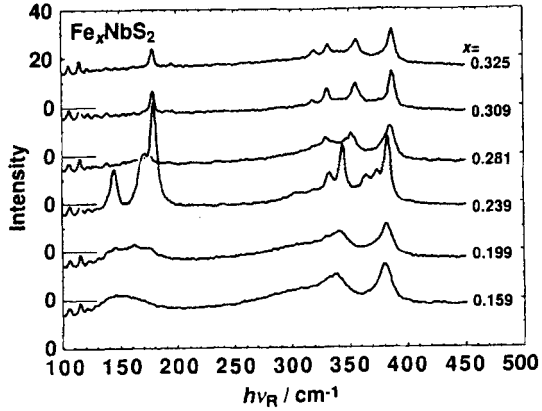

FIGURE 1 Depolarized Raman spectra of Fe_xNbS_2 at 300 K for various Fe contents x.

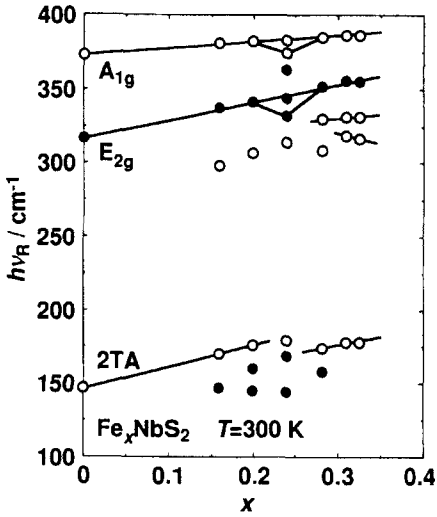

FIGURE 2 Phonon energies of Fe_xNbS_2 are plotted against Fe contents x; full circles are observed in both polarized and depolarized spectra, and open circles are observed in depolarized spectrum.

cusp at Néel temperature T_N=152 K; the highest transition temperature compared to the previous reports [1-4] indicates the higher quality of this sample. The orbital angular moment L of the intercalated Fe ion has not been quenched, because the susceptibility $\chi_{//}$ is larger than the $\chi_{\perp}$ in the paramagnetic region.

Assuming Curie-Weiss law in the paramagnetic region, we have estimated the effective moment μ_{eff} and paramagnetic Curie temperature θ. The obtained effective moments $\mu_{//}$ =2.7 μ_B and $\mu_{\perp}$ =3.0 μ_B are smaller than that of localized Fe^{2+} ion, where μ_B is the Bohr magneton; the small values suggest the itinerancy with the intercalated Fe 3*d* electrons. This itinerant picture is consistent of the small entropy change of specific heat at the T_N in Fe_xNbS_2 [8]. The Curie temperatures are $\theta_{\perp}$ = -47 K and $\theta_{//}$ = -7 K. We find that the $\theta_{\perp}$ and $\theta_{//}$ change their sign oscillatory as x increases. These results suggest that the

magnetic ordering in Fe_xNbS_2 can be attributed to the RKKY interaction between intercalated Fe ions via conduction electrons.

The glass temperature T_g and the Néel temperature T_N estimated by the magnetic susceptibilities increase from 13 K to 44 K with increasing x; these values correspond to the early result [5] except for x=0.239. It is very important that the Néel temperature (~150 K) at x=0.239 is enhanced drastically compared with other contents, whereas the Néel temperature at x=0.325 is 44 K.

From our Raman and magnetic measurements, we point out some correlations between the magnetic and structural properties induced by the Fe intercalation. When $x \leqq 0.199$, the intercalated Fe ions locate randomly at the octahedral sites, and show a spin glass state. In the samples with $0.281 \leqq x \leqq 0.325$, the antiferromagnetic ordering is accompanied by the cluster formation with $\sqrt{3}a \times \sqrt{3}a$ superstructure; the size of the clusters is enlarged with increasing x in this region. The $Fe_{0.239}NbS_2$ exhibits the $2a \times 2a$ superstructure and the antiferromagnetic ordering. In this content x~0.25, the RKKY interaction will be enhanced because the Fe configuration is arranged regularly in the van der Waals gap.

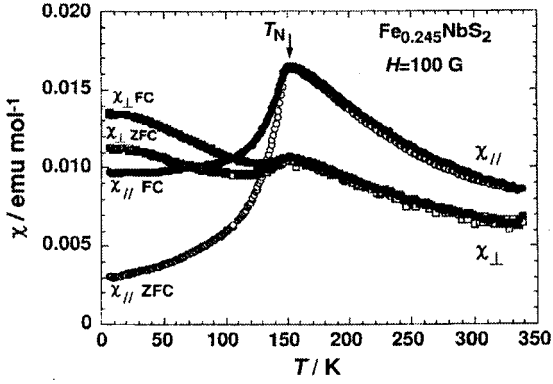

FIGURE 3 Temperature dependence of field cooling (FC) and zero field cooling (ZFC) magnetic susceptibilities for $Fe_{0.245}NbS_2$.

SUMMARY

We have obtained the experimental results of the Raman scattering and the magnetic susceptibility measurements in Fe_xNbS_2 ($0.159 \leqq x \leqq 0.325$). When $x \leqq 0.199$, the intercalated Fe ions locate randomly at the octahedral sites with spin glass state. In the samples with $0.281 \leqq x \leqq 0.325$ which indicate the antiferromagnetic ordering, the Fe ions form the cluster with $\sqrt{3}a \times \sqrt{3}a$ superstructure. The $2a \times 2a$ superstructure in x=0.239 (~ 0.25) is quite favorable to the appearance of an antiferromagnetic ordering than the $\sqrt{3}a \times \sqrt{3}a$ superstructure in the clusters.

At the content x=0.239, the magnetic guest and host phonon are coupled strongly. It suggests the possibility that some instabilities, such as CDW or spin density wave are induced by interactions among the intercalated Fe ions at the characteristic content.

Acknowledgments

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