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# Magnetic Phase Transitions in Pure and Cobalt-Doped Geometrically Frustrated $\text{Ni}_3\text{V}_2\text{O}_8$ Single Crystals

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The results of magnetic measurements performed on geometrically frustrated  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Ni}_{3(1-x)}\text{Co}_{3x}\text{V}_2\text{O}_8$  single crystals with  $x = 0.03$  are presented. It was found that Co doping did not change considerably the magnetic  $H-T$  phase diagram. Although no spin-glass effects were observed, nevertheless, a strong effect of 3 at% cobalt doping was evidenced. The main effect of Co-doping concerns the direction of the antiferromagnetic vector, which for  $\text{Ni}_3\text{V}_2\text{O}_8$  appears along the  $a$  axis, while for only slightly Co doped crystals — along the  $c$  axis. This switching of direction results from distinct changes of the magnetocrystalline anisotropy due to the presence of  $\text{Co}^{2+}$  ions strongly coupled to the kagome lattice. The disorder introduced by doping has practically no effect on the magnitude of the isotropic exchange interactions. At the same time the doping suppresses the Dzyaloshinskii–Moriya exchange interactions due to the change of direction of the antiferromagnetic vector.

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## 1. Introduction

The magnetic ions on kagome geometry lattice present one of the most highly frustrated two-dimensional quantum spin systems with only nearest-neighbor antiferromagnetic Heisenberg interactions. This type of magnetic materials is expected to exhibit a complex ground state and proximity to quantum phase transitions. The interest in geometrically frustrated systems is spurred

by the new phenomena predicted such as: noncollinear Néel long-range order, “order by disorder”, magnetization plateaus, and magnetization jumps. Recently, the isostructural compounds  $M_3V_2O_8$  ( $M = Ni, Co, Cu$ ) were shown to be new variants of kagome lattice (see [1–3] and references therein). In this lattice the planes that contain the edge sharing  $MO_6$  octahedra are not flat (as in the regular kagome lattice) but buckled forming a staircase-like structure. These kagome–staircase magnetic layers are separated by the non-magnetic  $VO_4$  tetrahedra. As a consequence the geometric frustration is reduced allowing for the existence of long-range magnetic order. The most of the studies performed so far were devoted until now to  $Ni_3V_2O_8$ . Using thermodynamic and neutron diffraction data the magnetic phase diagram was established for  $Ni_3V_2O_8$  single crystal [2, 3]. The transition from a paramagnetic to a high-temperature incommensurate (HTI) phase was shown to appear at  $T_{PH} = 9.1$  K. Then at  $T_{HL} = 6.3$  K this phase transforms into a low-temperature incommensurate (LTI) phase. Both phase transitions are continuous. Below  $T_{LC} = 3.9$  K the crystal displays two commensurate, slightly different canted antiferromagnet phases (C, C′). The transition at  $T_{LC}$  from the LTI phase to the one of these phases is discontinuous.

Since the disturbance of the delicate balance between the competing exchange interactions in frustrated magnets may lead to new effects, we decided to introduce chemical disorder to the kagome structure by Co-doping of  $Ni_3V_2O_8$  single crystals. In this paper we describe results of magnetic measurements performed on  $Ni_3V_2O_8$  (NVO) and  $Ni_{3(1-x)}Co_{3x}V_2O_8$  (NVO:3%Co) single crystals with  $x = 0.03$ .

## 2. Experimental results and discussion

The  $Ni_3V_2O_8$  and  $Ni_{3(1-x)}Co_{3x}V_2O_8$  single crystals were grown by a method of spontaneous crystallization. Magnetic measurements were performed for temperature from 2 K to 300 K in magnetic field up to 50 kOe using a commercial SQUID magnetometer (MPMS-5, Quantum Design). Figure 1a displays the low temperature dependences of the dc magnetic susceptibility,  $\chi = M/H$ , measured in magnetic field  $H = 100$  Oe applied along three crystallographic axes, for both NVO and NVO:3%Co. To make the figure more legible the scale of  $M/H$  is limited to 0.45 emu/(mol Oe). Therefore, the strong growth of the  $\chi(T)$  up to 9.15 emu/(mol Oe), measured for NVO at  $\mathbf{H} \parallel \mathbf{c}$  at low temperatures (below 3.9 K), is not visible. On the expanded scale Fig. 1b displays the  $\chi(T)$  for the NVO:3%Co crystal at  $\mathbf{H} \parallel \mathbf{c}$ , so that the peculiarities of  $\chi(T)$  are visible. The positions of the phase transitions for  $Ni_3V_2O_8$  are very close to those reported in [2, 3]. The two of them, namely transitions at  $T_{HL} = 6.5$  K and  $T_{CC'} = 2.6$  K are points of second-order phase transitions while the sharp transition at  $T_{LC} = 3.9$  K is a first-order one. The transition observed in  $Ni_3V_2O_8$  at  $T_{PH} = 9.1$  K between a paramagnetic (P) and a HTI phase is not seen in our  $\chi(T)$  data. It is also not seen

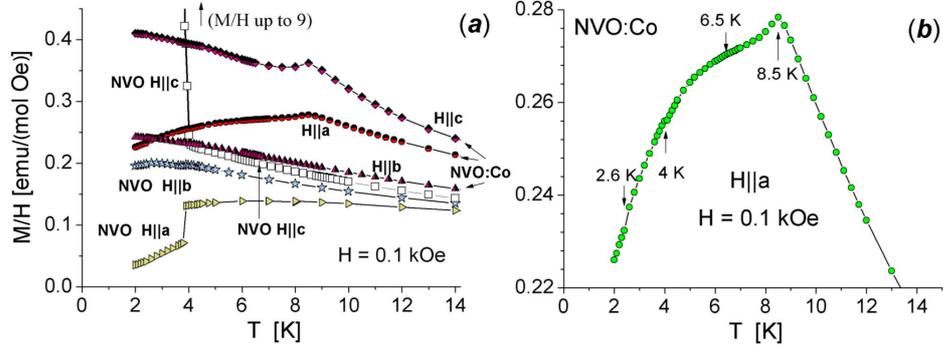


Fig. 1. (a) Low temperature dependences of magnetic susceptibility measured in magnetic field  $H = 100$  Oe applied along three crystallographic axes for  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Ni}_3\text{V}_2\text{O}_8:3\%\text{Co}$  crystals. (b) Peculiarities in  $\chi(T)$  dependence for  $\text{Ni}_3\text{V}_2\text{O}_8:3\%\text{Co}$  at  $H \parallel a$ .

in magnetic data presented in [2, 3]. This transition is revealed in specific heat and neutron scattering experiments. The doping by Co ions makes all transitions a little shifted, in comparison with those in undoped samples. Moreover, the characteristic sharp transition  $\text{LTI} \rightarrow \text{C}$  observed in  $\text{Ni}_3\text{V}_2\text{O}_8$  practically disappears in doped crystals. Magnetic phase transitions observed in doped crystals seem to be of the second order. Taking into account that both the samples have the same crystal structure and close crystal lattice parameters, it could be assumed that the phase diagrams for low doped crystals are similar to those determined for  $\text{Ni}_3\text{V}_2\text{O}_8$ . This point is supported by the observation [1] that phase diagrams for  $\text{Ni}_3\text{V}_2\text{O}_8$  and for  $\text{Co}_3\text{V}_2\text{O}_8$  are very similar. It means that the transitions for the NVO:3%Co sample seen at  $T = 8.5$  K, 6.5 K, 4 K, and 2.6 K should be identified as  $\text{P} \rightarrow \text{HTI}$ ,  $\text{HTI} \rightarrow \text{LTI}$ ,  $\text{LTI} \rightarrow \text{C}$  and  $\text{C} \rightarrow \text{C}'$ , respectively. The paramagnetic phase for  $T > T_{\text{PH}} = 8.5$  K was identified by magnetization measurements  $M(H)$ . The other phases were recognized on the base of the postulated similarity between doped and undoped crystals. The characteristic feature of the phase diagram of NVO:3%Co crystals is its remarkable anisotropy. The anisotropy of the magnetic properties is also seen in the paramagnetic phase. Figure 2 presents the reciprocal of magnetic susceptibility  $H/M$  as a function of temperature, for  $T > 50$  K, in magnetic field  $H = 1$  kOe applied along the  $a$ ,  $b$ , and  $c$  axes for both NVO and NVO:3%Co single crystals. The temperature dependence  $\chi(T)$  can be well described by the Curie–Weiss law in the wide temperature range ( $T > 100$  K) with the paramagnetic Curie–Weiss temperatures being equal to:  $\theta_a = -15.6$  K,  $\theta_b = -17.4$  K,  $\theta_c = -15.4$  K for  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\theta_a = -11.6$  K,  $\theta_b = -31.4$  K,  $\theta_c = -7.51$  K for NVO:3%Co. Generally, the paramagnetic Curie temperature,  $\theta_j$ , is determined by the exchange interactions between magnetic ions as well as by the crystal field acting on magnetic ions. The contribution of the exchange interactions is proportional to parameter  $\theta = \theta_a + \theta_b + \theta_c$ . The obtained results indicate

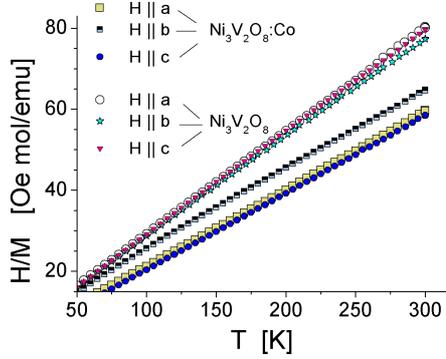


Fig. 2. Reciprocal magnetic susceptibility of  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Ni}_3\text{V}_2\text{O}_8:3\%\text{Co}$  crystals in paramagnetic region.

that the low doping has practically no effect on  $\theta$ , but it changes considerably the anisotropy of  $\theta_j$  parameters. Consequently, the low doping does not change the frustration determined by antiferromagnetic exchange interactions in the system, but it has a strong influence on the magnetocrystalline anisotropy determined by the crystal field interactions.

The effective magnetic moments  $P_{\text{eff}}$  determined for magnetic ion have values:  $P_{\text{eff}}^a = 3.24 \mu_{\text{B}}$ ,  $P_{\text{eff}}^b = 3.30 \mu_{\text{B}}$ ,  $P_{\text{eff}}^c = 3.24 \mu_{\text{B}}$  for NVO and  $P_{\text{eff}}^a = 3.74 \mu_{\text{B}}$ ,  $P_{\text{eff}}^b = 3.68 \mu_{\text{B}}$ ,  $P_{\text{eff}}^c = 3.75 \mu_{\text{B}}$  for NVO:3%Co. They are noticeably larger than those predicted for a spin-only system ( $2.83 \mu_{\text{B}}/\text{Ni}^{2+}$ ) and in the case of  $\mathbf{H} \parallel (a, b)$  for Co-doped crystal they are close to a spin-only pure Co system ( $3.87 \mu_{\text{B}}/\text{Co}^{2+}$ ). It is probably due to the distinct orbital contribution to the overall moment indicating that even in the case of  $\text{Ni}^{2+}$  the orbital moment is not quenched.

The influence of a magnetic field on magnetization of both the systems was studied for three different field orientations:  $\mathbf{H} \parallel \mathbf{a}$ ,  $\mathbf{H} \parallel \mathbf{b}$ , and  $\mathbf{H} \parallel \mathbf{c}$ . Measurements of magnetization curves in NVO and NVO:3%Co at 2 K (Fig. 3a and b) confirm a strong magnetic anisotropy of both materials. It is also seen that the doping changes considerably the character of this anisotropy. First of all, the magnetization for NVO:3%Co is higher than for undoped  $\text{Ni}_3\text{V}_2\text{O}_8$ . It has to be related to the decrease in the exchange interactions due to the  $\text{Co}^{2+}$  doping. The highest value of magnetization at  $T = 2$  K is observed for  $\mathbf{H} \parallel \mathbf{c}$  for both crystals.

In agreement with high temperature magnetic measurements indicating on antiferromagnetic interactions between magnetic ions, in the low temperature region the antiferromagnetic component of the magnetization dominates for  $H \approx 0$ . Only for  $\mathbf{H} \parallel \mathbf{c}$  in  $\text{Ni}_3\text{V}_2\text{O}_8$  (Fig. 3a) a weak ferromagnetic moment exists due to the Dzyaloshinskii–Moriya exchange interactions. Figure 3b evidences that the doping suppresses strongly this interaction.

Figure 4 presents the  $M(H)$  dependences for both samples measured at 2 K and 3 K in the magnetic field applied along the  $a$  axis. In both cases the magnetization curves are typical of antiferromagnetic phase. For  $\text{Ni}_3\text{V}_2\text{O}_8$  the spin-flop

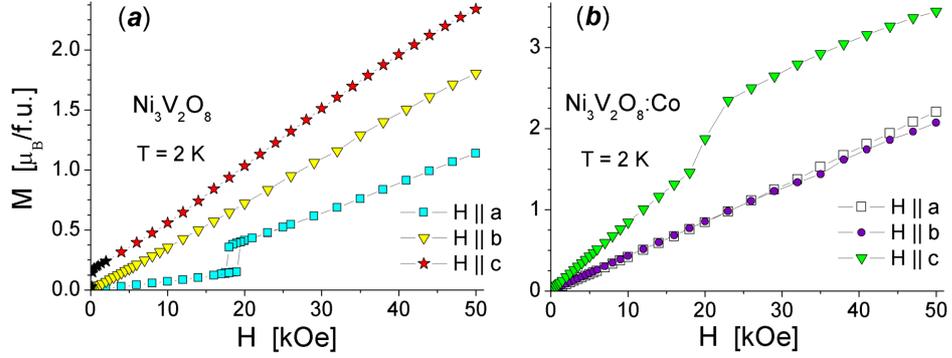


Fig. 3. Magnetization curves at 2 K for (a)  $\text{Ni}_3\text{V}_2\text{O}_8$  and (b)  $\text{Ni}_3\text{V}_2\text{O}_8:3\%\text{Co}$  crystals. Magnetic field was applied along three crystallographic axes.

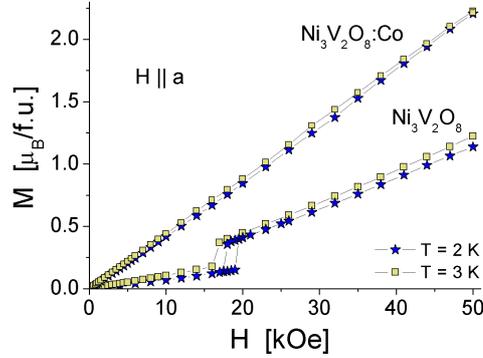


Fig. 4. Magnetization curves at 2 K and 3 K for both samples in magnetic field  $\mathbf{H} \parallel \mathbf{a}$ .

first-order phase transition with a noticeable field hysteresis is clearly seen. It means that the easy magnetization axis and the direction of antiferromagnetic vector are directed along the  $a$  axis. With decreasing temperature this transition shifts to higher fields. The spin-flop transition is not seen in doped crystals. In contrast to this case for the magnetic field applied along the  $b$  axis (Fig. 5) the field-induced phase transition is observed in  $\text{NVO}:3\%\text{Co}$  crystal, while it is not seen in  $\text{Ni}_3\text{V}_2\text{O}_8$  crystal (not shown). This phase transition is very broad, nevertheless the hysteresis is clearly expressed indicating the first-order character of the transition. This transition shifts to higher fields with an increase in temperature. It should be stressed that the system behavior is typical of antiferromagnets, before and after the phase transition, and that the ferromagnetic moment (extrapolated to  $H = 0$ ) is within the experimental error equal to zero. It means that it is not a transition of the spin-flop type. This magnetic field-induced phase transition has an origin similar to that established in  $\text{Co}_3\text{V}_2\text{O}_8$  [1] for magnetic field  $\mathbf{H} \parallel \mathbf{b}$ . In this case in the absence of external magnetic field, the antiferromagnetic vector is not parallel exactly to the  $c$  axis, but makes a small angle with it. In a sufficiently

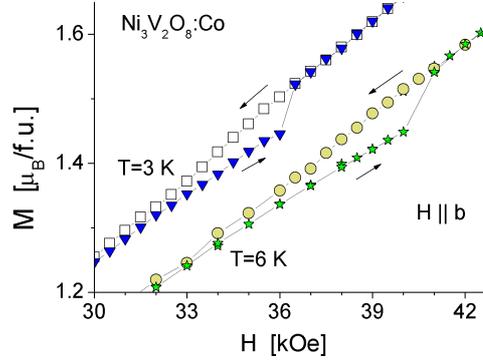


Fig. 5. Magnetization curves at 3 K and 6 K for  $\text{Ni}_3\text{V}_2\text{O}_8:3\%\text{Co}$  crystal in magnetic field  $\mathbf{H} \parallel \mathbf{b}$ .

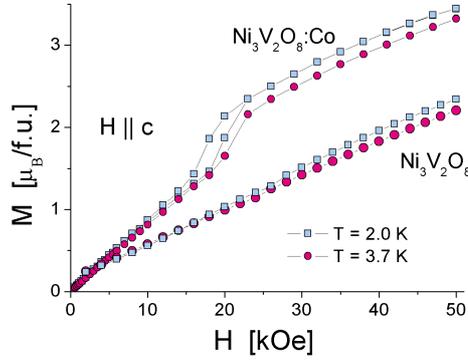


Fig. 6. Magnetization curves at 2 K and 3.7 K for both samples in magnetic field  $\mathbf{H} \parallel \mathbf{c}$ .

strong magnetic field the reorientation of spins is induced leading to the situation when the antiferromagnetic vector becomes parallel to the  $c$  axis.

A quite different situation exists for both crystals when the magnetic field is applied along the  $c$  axis (Fig. 6). For this orientation the field-induced phase transition also exists only in  $\text{NVO}:3\%\text{Co}$  crystal in a low temperature region (below 7.5 K). In full analogy to the  $\mathbf{H} \parallel \mathbf{b}$  case the observed transition is of the first-order one with a weakly expressed hysteresis. But in this case the ferromagnetic moment (extrapolated to  $H = 0$  after the phase transition) is not equal to zero. It means that it is a transition of the spin-flop type and that for the doped crystal the easy magnetization axis and the direction of antiferromagnetic vector are directed along the  $c$  axis.

### 3. Conclusions

We present here first observations of the effect of chemical disorder on geometrically frustrated kagome systems. Such systems have never been studied

theoretically although several papers have been recently devoted to the problem of impurities in the two-dimensional  $s = 1/2$  Heisenberg antiferromagnets (see [4–7] and references therein). These studies indicate that the impurities can dramatically affect the ground state of the host materials. The presence of frustration often leads to a spin-glass state.

In the geometrically frustrated kagome  $\text{Ni}_3\text{V}_2\text{O}_8$  crystals studied here the Co doping does not change considerably a magnetic phase diagram. No evidence of the spin-glass effects are observed. At the same time a strong effect of Co-doping is noted, related to a strong spin–lattice coupling, as expected for  $\text{Co}^{2+}$  ions in the kagome lattice. The main effect of Co-doping is to switch the direction of the antiferromagnetic vector, which for  $\text{Ni}_3\text{V}_2\text{O}_8$  is parallel to the  $a$  axis, while for NVO:Co it is parallel to the  $c$  axis. The difference in the antiferromagnetic vector direction results from large changes of the magnetocrystalline anisotropy due to the presence of  $\text{Co}^{2+}$  ions strongly coupled to the lattice. The same effect is also responsible for the anisotropy of the paramagnetic Curie temperatures, which increases with Co ions doping.

The disorder introduced by doping has practically no effect on the magnitude of the Heisenberg exchange interactions. A puzzling effect of suppressing the Dzyaloshinskii–Moriya exchange interactions should be related to the change of antiferromagnetic vector direction due to doping.

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