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## LETTER TO THE EDITOR

## Single crystals of the anisotropic Kagomé staircase compounds $\text{Ni}_3\text{V}_2\text{O}_8$ and $\text{Co}_3\text{V}_2\text{O}_8$

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### Abstract

Compounds with a Kagomé type lattice are known to exhibit magnetic frustration. Large single crystals of two compounds,  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$ , which are variants of a Kagomé net lattice, have been grown successfully by the floating zone technique using an optical image furnace. The single crystals are of high quality and exhibit intriguing magnetic properties.

For a considerable time now, the Kagomé type lattice has been the corner stone of theoretical investigations of highly frustrated magnetic systems. This is because a nearest-neighbour antiferromagnet on a Kagomé lattice (a net of corner sharing triangles) has an infinitely large number of classical ground states; the system remains a disordered spin liquid down to zero temperature, reflecting this macroscopic degeneracy. From an experimental perspective, however, finding a perfect example of a 2D Kagomé lattice has proved to be difficult, as even weak residual 3D interactions or magnetic anisotropy can lead to an ordered or glassy state.

Among the Kagomé-like systems, the best known and well investigated example is  $\text{SrGa}_4\text{Cr}_8\text{O}_{19}$  [1], while more recently a mineral volborthite,  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [2],  $\text{Ba}_2\text{Sn}_2\text{ZnCr}_{7p}\text{Ga}_{10-7p}\text{O}_{22}$  [3] and different jarosites [4] have been advanced as Kagomé type lattices (for a recent review of the chemistry and synthesis of frustrated magnets, including the Kagomé type, see [5]).

In this letter we describe the growth of single crystals of two isostructural compounds,  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$ , by the floating zone technique. The compounds  $\text{M}_3\text{V}_2\text{O}_8$ , where  $\text{M} = \text{Ni}$  and  $\text{Co}$ , are new variants of the Kagomé lattice, where the planes that contain the edge sharing  $\text{MO}_6$  octahedra are no longer flat, but buckled to form a staircase-like structure [6, 7]. This staircase of magnetic layers separated by the non-magnetic  $\text{VO}_4$  tetrahedra results in a reduction in the geometric frustration and therefore long-range magnetic order has been observed in both  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$  [6]. While small crystals of both these compounds

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**Figure 1.** Photograph of the as-grown boules of  $\text{Ni}_3\text{V}_2\text{O}_8$  (left) and  $\text{Co}_3\text{V}_2\text{O}_8$  (right) grown by the floating zone technique.

have been grown, from the melt, for crystal structure studies [8], large single crystals have not been grown so far. The magnetic properties of both the Ni and the Co compounds have been reported only for polycrystalline powder samples [6]. Neither the exact nature of the observed magnetic transitions nor the magnetic ground state of these compounds has yet been investigated. In view of the interesting magnetic properties these lattices exhibit, it is desirable to carry out investigations on good quality single crystals. Initial characterization of the grown crystals by x-rays and magnetic susceptibility measurements is also presented in this letter.

Both  $\text{Co}_3\text{V}_2\text{O}_8$  and  $\text{Ni}_3\text{V}_2\text{O}_8$  adopt orthorhombic crystal structures, space group  $Cmca$  [8]. Polycrystalline materials were first prepared by the solid state reaction of the starting oxides. High purity NiO, CoO and  $\text{V}_2\text{O}_5$  were taken in stoichiometric ratios and mixed well together. The mixtures were reacted in air at  $800^\circ\text{C}$  for a day. The Ni compound was further heated at  $900^\circ\text{C}$  for a day, while the Co compound was heated at  $1050^\circ\text{C}$  for two days. Both powders were ground in between each firing to ensure good homogeneity of the mixture. The polycrystalline powders were checked for the correct phase formation and purity using x-ray powder diffraction. The powders were then isostatically pressed to produce rods roughly 7–8 mm in diameter and 70–80 mm long. The rods were sintered in air at 900 and  $1050^\circ\text{C}$  for the Ni and the Co compounds respectively and used for crystal growth. Crystal growth was carried out by the floating zone technique [9] in a four-mirror image furnace (CSI model FZ-T-1000-H-IV-VPS). The crystal growth was carried out at growth speeds ranging from  $0.5$  to  $3\text{ mm h}^{-1}$ , with the seed and feed rods rotating at 20–30 rpm. All the growths were carried out in air at ambient pressure. A polycrystalline seed rod was used for the first growth and the crystal obtained was used as the seed for subsequent growths.

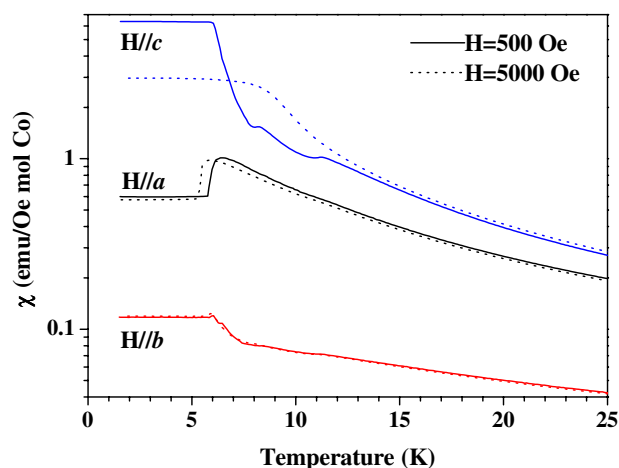
X-ray Laue photographs were taken to check crystal quality and to align the crystals. Magnetic susceptibility measurements were carried out using an Oxford Instruments vibrating sample magnetometer (VSM).

Both  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$  have congruent melting points and therefore their crystal growth by the floating zone technique posed no problems. The crystals developed shiny facets as they grew. The  $\text{Ni}_3\text{V}_2\text{O}_8$  crystal was dark with a greenish hue while the  $\text{Co}_3\text{V}_2\text{O}_8$  crystal was black. Photographs of both the as-grown crystal boules are shown in figure 1, illustrating the size and volume of the crystals that can be grown by this method. The quality of the crystals was checked using x-ray Laue back-reflection photographs. A typical photograph obtained from a crystal of  $\text{Co}_3\text{V}_2\text{O}_8$  is shown in figure 2. A few of the crystals grown have also been examined using neutron Laue photographs, which have shown that the crystals are suitable for future inelastic neutron scattering experiments.

Slices were cut from the boule for various measurements and a portion of the boule was used to obtain pieces oriented along the three principal crystallographic axes for measurements. Below, we present our initial measurements of the magnetic properties of one of the crystals



**Figure 2.** X-ray Laue back-reflection photograph of a crystal of  $\text{Co}_3\text{V}_2\text{O}_8$  showing the (100) orientation.



**Figure 3.** Temperature dependence of the magnetic susceptibility of a single crystal of  $\text{Co}_3\text{V}_2\text{O}_8$  measured with the magnetic field applied along the three different directions.

(This figure is in colour only in the electronic version)

grown, namely,  $\text{Co}_3\text{V}_2\text{O}_8$ . The magnetic susceptibility ( $\chi$ ) of a crystal of  $\text{Co}_3\text{V}_2\text{O}_8$  measured in an applied field of 500 Oe and 5 kOe using the VSM is shown in figure 3. In agreement with the results of the magnetic susceptibility measurements on powder samples [6], the susceptibility is almost Curie–Weiss-like at higher temperatures, but small deviations from  $\frac{C}{T-\Theta}$  make the accurate determination of the Weiss constant  $\Theta$  difficult.

The measurements on the  $\text{Co}_3\text{V}_2\text{O}_8$  single crystals for  $H \parallel a$ ,  $H \parallel b$  and  $H \parallel c$  reveal the presence of a large magnetic anisotropy in this compound. As can be seen from figure 3, the direction of the easy-axis magnetization in  $\text{Co}_3\text{V}_2\text{O}_8$  is along the  $c$ -axis, while the hard axis

is parallel to  $b$ . Remarkably, the ratio of the magnetic susceptibilities for  $H \parallel c$  and  $H \parallel b$  exceeds a factor of 50 at low temperatures. The susceptibility  $\chi_{\parallel c}(T)$  curve shows a sharp increase at a temperature around 6.0 K, below which it remains nearly constant, similar to the powder data [6]. It also shows two clear anomalies at  $T = 8.2$  and 11.2 K, while only one has been seen in powder samples [6]. Both these anomalies  $T = 8.2$  and 11.2 K are also evident in the corresponding  $\chi_{\parallel b}(T)$  curve, which also reaches its maximum value at  $T = 6.0$  K and remains constant at lower temperatures. In sharp contrast, the  $\chi_{\parallel a}(T)$  curve does not show any anomalies at higher temperatures; it reaches its maximum at a temperature of  $T = 6.4$  K and then decreases rapidly by about 40% before becoming temperature independent below  $T = 5.7$  K.

The magnetic susceptibilities for all three directions of applied field are quite sensitive to the field values used, with the easy-axis susceptibility  $\chi_{\parallel c}(T)$  being most affected at the higher field (see the dashed curves in figure 3). This observation suggests that  $\text{Co}_3\text{V}_2\text{O}_8$  may have a complicated  $H$ - $T$  phase diagram.

Heat capacity measurements reported on powder samples of  $\text{Ni}_3\text{V}_2\text{O}_8$  indicate that it exhibits four transitions above 2 K, while the corresponding magnetic susceptibility measurement shows no indication of two of these transitions (at 6 and 9 K) [6]. It will be interesting to see whether the measurements of magnetic susceptibility on single-crystal samples provide more detailed information on the series of the phase transitions in  $\text{Ni}_3\text{V}_2\text{O}_8$ .

In contrast to the multiple phase transitions exhibited by  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$ , the third member of the family,  $\beta$ - $\text{Cu}_3\text{V}_2\text{O}_8$ , is reported to undergo a single 3D magnetic transition at  $\sim 29$  K with indications of short-range or low-dimensional ordering at higher temperatures [7]. The magnetic properties of  $\beta$ - $\text{Cu}_3\text{V}_2\text{O}_8$  have been investigated only in powder form; further progress in the understanding of its magnetic properties would undoubtedly benefit from the manufacture of single-crystal samples.

In conclusion, large high-quality crystals of the Kagomé staircase lattices  $\text{Ni}_3\text{V}_2\text{O}_8$  and  $\text{Co}_3\text{V}_2\text{O}_8$  have been grown by the floating zone technique. This method is ideally suited for the crystal growth of this interesting class of compounds, especially where large volumes are required for the investigation of their magnetic properties by neutron scattering experiments. The magnetic properties measured here on single-crystal samples of  $\text{Co}_3\text{V}_2\text{O}_8$  for the first time show a huge anisotropy. Specific heat and magnetization measurements have been carried out on these crystals and will be reported separately. Detailed investigations of the nature of the magnetic transitions in these crystals are planned using neutron scattering experiments.

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