

WATER-INDUCED AND Co-FILLING CONTROL INDUCED FERROMAGNETISM IN $\text{Rb}_2\text{Ni}_3\text{S}_4$

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The influence of water-immersing on the magnetic behavior of $\text{Rb}_2\text{Ni}_3\text{S}_4$ single crystals grown by the flux method was studied, where the intrinsic substance is non-magnetic because of the low spin state of Ni^{2+} in a Kagome lattice. The influence of Co-doping to $\text{Rb}_2\text{Ni}_3\text{S}_4$ was also studied in terms of the local spin density approximation (LSDA) band structure calculation. Residual ferromagnetic moments appeared in specimens immersed into water, as their magnitudes increase depending on the immersion time. The LSDA band structure calculation suggested that Co substitution for Ni allows deriving a novel ferromagnetic behavior.

INTRODUCTION

Transition metal Ni sulfides represented by NiS and NiS₂ are important materials to study physics of the systems involving strong electron correlation, for instance, the metal-insulator transition, the mechanism responsible for which has been a subject of great interest [1-3]. $\text{Rb}_2\text{Ni}_3\text{S}_4$ dealt here is one of a series of layered ternary Ni sulfides $\text{A}_2\text{Ni}_3\text{S}_4$ (A = K, Rb, Cs) [4], having a substantially flat-bands immediately below the Fermi Level [5]. The recent photoemission spectroscopy has revealed that $\text{Rb}_2\text{Ni}_3\text{S}_4$ is a moderately correlated, strongly *p-d* hybridized system [6].

The crystal structure of this system was reported to be a face centered-orthorhombic structure with the space group Fmmm [7]. The characteristic feature is that Ni ions constitute a Kagome lattice sandwiched by two S honeycomb lattices so as to form stacked packages (figure 1) [8]. Each Ni ion is located at the center of the S₄ squares, which link together to form six-membered rings. Motivated by the interest in this crystal structure for transition metal Ni sulfides, the present author's group performed a study of magnetic and electronic properties of $\text{Rb}_2\text{Ni}_3\text{S}_4$. As a result, Ni^{2+} on the present Kagome lattice was found to take a low-spin state being non-magnetic. However, the specimens of single crystal grown by the flux method was found to be very weak ferromagnetic exclusively under washing off the flux with water [5]. This finding is very interesting, because layered structures of Alkali metal compounds can be sensitive to intercalation. Superconductivity was recently discovered in $\text{Na}_x\text{CoO}_2 \cdot n(\text{H}_2\text{O})$ [9], where the water

intercalation in the layered structure can play an important role. In addition, a flat-band of the electronic state on Kagome lattice has been known to be able to derive ferromagnetism [10].

Therefore, it is important to investigate the influence of water on $\text{Rb}_2\text{Ni}_3\text{S}_4$ for obtaining a comprehensive understanding of the magnetic and electronic properties of this layered Ni sulfide and to clarify the effect of Co^{2+} -doping on the host $\text{Rb}_2\text{Ni}_3\text{S}_4$ for examining a flat-band magnetism on real substances. In the present study we attempted to derive ferromagnetism in $\text{Rb}_2\text{Ni}_3\text{S}_4$ through both an immersion treatment of single crystals and the local spin density approximation (LSDA) band structure calculation on Co-filling control for $\text{Rb}_2\text{Ni}_3\text{S}_4$. The experimental results show that the water-immersion enhances residual magnetic moments. The theoretical results predict that one-third substitution of Co for Ni demonstrates a half metallic ferromagnetism.

EXPERIMENTAL

Single crystals of $\text{Rb}_2\text{Ni}_3\text{S}_4$ were grown by a flux method starting from Rb_2CO_3 (99%), Ni (99%), and S (99%), mixed in the ratio of 5:1:12 mole. The mixture was put in an Al_2O_3 99.8% alumina crucible and heated in a combustion tube with flowing argon gas. The furnace was heated at 9°C/min to 850°C, held at this tem-

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perature for 3 hours and then cooled to room temperature by furnace cooling. In order to remove the flux, the surface of the crystal was mechanically peeled off without using water. In the present study, in order to know the influence of water on specimens of $\text{Rb}_2\text{Ni}_3\text{S}_4$, some of obtained specimens were immersed into water for different time, and then dried in vacuum for the same time. The samples were in the shape of shiny thin foil approximately $10 \times 10 \times 0.015$ mm so as to reflect quasi-two-dimensional layer crystals.

Specimens of Co-doped $\text{Rb}_2\text{Ni}_3\text{S}_4$, that is, $\text{Rb}_2(\text{Co}_x\text{Ni}_{1-x})_3\text{S}_4$ ($0 < x < 1$), were also grown by a flux method starting from Rb_2CO_3 (99%), Co (99%), Ni (99%), and S (99%), mixed in the ratio of 5 : x : $1-x$: 12 mole. Various range of x ($0 < x < 1$) was attempted for preparation. Other details of preparation for $\text{Rb}_2(\text{Co}_x\text{Ni}_{1-x})_3\text{S}_4$, that is, temperature condition and so on, were same to that for $\text{Rb}_2\text{Ni}_3\text{S}_4$. In order to remove the flux, the surface of the crystal was also mechanically peeled off without using water. The samples were also in the shape of shiny thin foil approximately $8 \times 8 \times 0.015$ mm so as to reflect quasi-two-dimensional layer crystals. The level of Co-substitution was estimated magnetically by fitting to $1/\chi(T)$ plot, as described hereafter. This is because the amount of Co ion was small, and therefore scanning electron microscopy (SEM) analysis, the resolution of which was approximately 1% in molar ratio of atomic existence, failed to obtain confident values of Co concentration. The obtained molar ratio of Co ion to total Rb, Co, Ni, and S ions were typically less than 1%.

X-ray diffraction patterns were taken at room temperature with a Philips PW1700 diffractometer to confirm the identity of specimens. The monochromatized X-ray source $\text{Cu K}\alpha_1$ $\lambda = 1.540 \text{ \AA}$ and $\text{Cu K}\alpha_2$ $\lambda = 1.544 \text{ \AA}$ was employed. In the measurements, a specimen in sheet was placed on a plane measuring stage. Since scanning plane is perpendicular to a plane of specimen, diffraction patterns of sheeted specimens were limited to the reflections mainly from the Miller

planes perpendicular to the scanning plane. A calculated pattern of X-ray diffraction for $\text{Rb}_2\text{Ni}_3\text{S}_4$ was obtained by applying the crystallographic data of $\text{Rb}_2\text{Ni}_3\text{S}_4$, that is, the space group $Fm\bar{3}m$ [7] and lattice constants $a = 9.901 \text{ \AA}$, $b = 13.606 \text{ \AA}$, and $c = 5.861 \text{ \AA}$ [7], to CrystalDiffract [11].

All magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS XL). The magnetic susceptibilities were measured at 1000 G, and the magnetizing processes as a function of external field up to 7 T were measured at 2 K. In all measurements, magnetic fields were applied parallel to the b axis.

Resistivity measurements were performed at temperature from 1.8 K to 773 K. Different sample holders were used according to the temperature range. The specimens were prepared in two ways for measuring the resistivity perpendicular and parallel to the b axis of the crystals. For the measurement parallel to the b axis, Au was evaporated on each side of the (010) surface of the specimen, and for the measurement perpendicular to the b axis, Au was evaporated on the same side of the (010) surface with an interval of approximately 1 mm. Ag wires were fixed on the respective electrodes with Ag paste.

The density of states (DOS) for $\text{Rb}_2\text{CoNi}_2\text{S}_4$: $\text{Rb}_2(\text{Co}_x\text{Ni}_{1-x})_3\text{S}_4$ ($x = 0.33$), was calculated in terms of the full-potential linearized augmented plane-wave (FLAPW) method based on the local spin density approximation (LSDA) by the present author (Usuda). The reported lattice constants $a = 9.901 \text{ \AA}$, $b = 13.606 \text{ \AA}$, and $c = 5.861 \text{ \AA}$ [7] were used in the calculation. There is no literature on the atomic position parameters of Rb and S atoms, but $\text{Cs}_2\text{Ni}_3\text{Se}_4$ belongs to the same space group as $\text{Rb}_2\text{Ni}_3\text{S}_4$, and hence we evaluated their appropriate values from the data of $\text{Cs}_2\text{Ni}_3\text{Se}_4$ [7] on the basis of the similarity of the crystal lattice. The muffin-tin radii of Rb, Co, Ni, and S were set to be 3.0, 2.3, 2.3, and 1.8 a.u., respectively. The Rb $(4p)^6(5s)^1$, Co $(3d)^7(4s)^2$, Ni $(3d)^8(4s)^2$, and S $(3s)^2(3p)^4$ electrons were treated as valence electrons. In these calculations, 365 k points were used in the irreducible Brillouin zone, which correspond to 2048 k points in the first Brillouin zone.

RESULTS AND DISCUSSION

The crystal qualities of the specimens prepared were examined by X-ray diffraction. The sample dependence of X-ray diffraction patterns is shown in figure 2. Diffraction from the planes perpendicular to the b axis was mainly observed. Since the diffraction peaks assigned to (131), (262), and (191) were observed in the figure owing to their strong intensity, a small amount of misaligned crystallites may be involved.

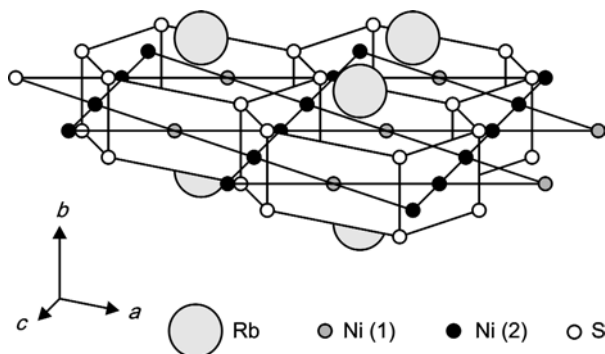


Figure 1. Stacked package of $\text{Rb}_2\text{Ni}_3\text{S}_4$. Ni ions constitute a Kagome lattice layer which is perpendicular to the b axis.

As shown in figure 2, the diffraction angles of all samples agree well with each other, and no significant lines indicating the presence of an impurity phase was found in either. Thus, the water cannot play a significant role in modifying the crystal structure or producing contaminations. However, the diffraction line width in diffraction profiles becomes broader depending on the prolonged immersion. For example, the full-width in half-maxima (FWHM) in (020) reflection, which appeared around $2\theta = 12.98^\circ$ in figure 2, was evaluated to $\Delta 2\theta = 0.09^\circ$, 0.18° , and 0.31° , with respect to specimen without water, immersed for 5 hours, and immersed for 10 hours, respectively. Thus, it is suspected that water molecules intercalate into the interstitial between stacked packages and partially disturb the lattice commensurability.

Experimental results of the immersion dependence of the magnetic properties in $Rb_2Ni_3S_4$ are shown in figures 3 and 4. In figure 4, the magnitude of magnetization of the sample immersed into water for 300 minutes is divided by 10 for the purpose of illustrative view.

As shown in figure 3, the magnetic susceptibility increases with decreasing temperature, and the magnitude of the magnetization develops with increasing

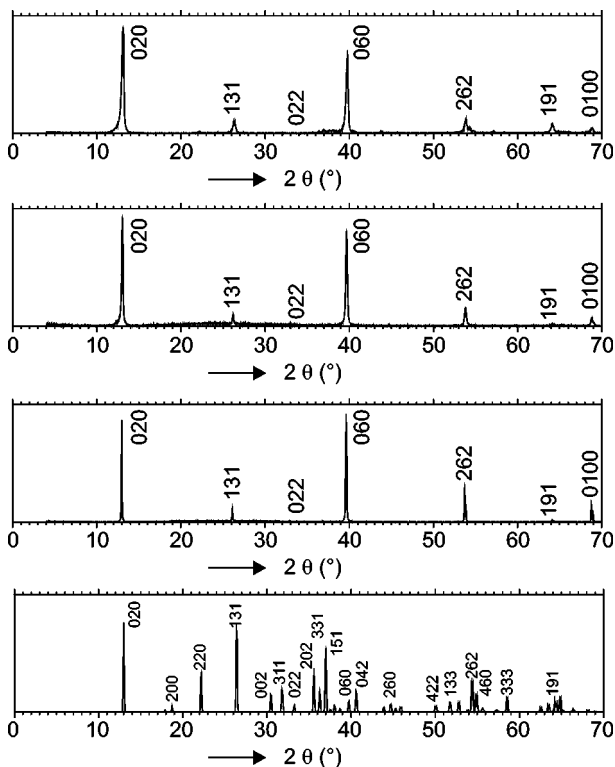


Figure 2. X-ray diffraction patterns of prepared specimens of $Rb_2Ni_3S_4$. The patterns of calculation, a specimen without water, a specimen immersed into water for 5 hours, and a specimen immersed for 10 hours are represented in the lowest panel, second lower, third lower, and the upper, respectively.

immersion time. As shown in figure 4, the residual magnetic moments, which are very small (on the order of about 1/100 to 1/1000 in comparison with the moment $2.28 \mu_B$ of Ni^{2+} with $S = 1$ spin), and the magnetic hysteresis are observed for the samples immersed into water.

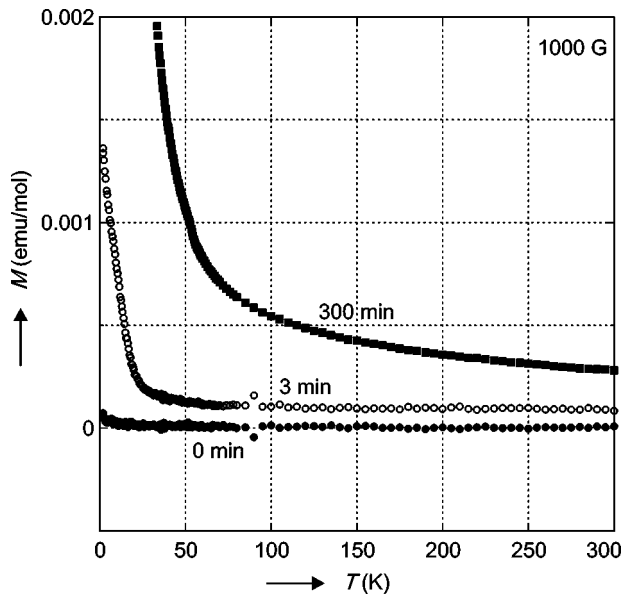


Figure 3. The plots of magnetization vs. temperature. Sample dependence of magnetization at 1000 G. The temperature dependence of magnetization for samples immersed into water for varying time is shown.

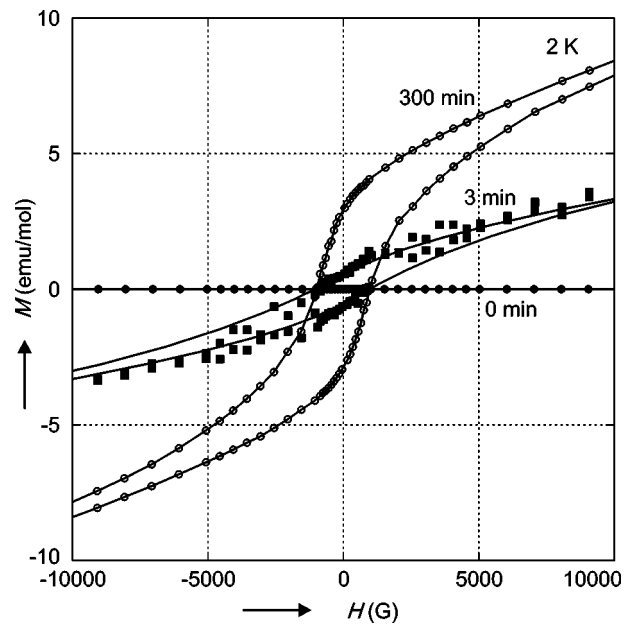


Figure 4. The plots of magnetization vs. magnetic field. Sample dependence of magnetization at 2 K. M vs. H curves for the samples immersed into water for various hours are represented. The magnitude of magnetization for 300 min is divided by 10.

As previously described, since there is not any significant impurity in each sample immersed into water, those magnetic features are not ascribed to be due to the presence of magnetic impurities. According to the experimental results of X-ray diffraction, the samples immersed into water have broader diffraction lines. Therefore, it can be understood that lattice distortions may occur in places, and that the defects of Rb and/or S may present. Because, if there are some lattice distortions and some defects of S, the square planar coordination of sulfur can be destroyed, and then magnetic moments of Ni can appear, and if there are some defects of Rb, there is a possibility that total charge balance of $\text{Rb}_2\text{Ni}_3\text{S}_4$ is modified, and then magnetic moments of Ni can appear owing to a possible change in the valence of Ni.

On a reflection on the presence of Kagome lattice layers, $\text{Rb}_2\text{Ni}_3\text{S}_4$ can have a flat band mainly consisting of Ni 3d bands below the Fermi level [5]. Since Ni 3d bands below the Fermi level have high density of states, there is a possibility that ferromagnetism is induced by controlling the filling at Ni site. Here, in order to examine such ferromagnetism in $\text{Rb}_2\text{Ni}_3\text{S}_4$, the effect of Co substitution for Ni was studied based on the LSDA band structure calculation to.

Figure 5 shows a result of the LSDA band structure calculation for $\text{Rb}_2\text{CoNi}_2\text{S}_4$: $\text{Rb}_2(\text{Co}_x\text{Ni}_{1-x})_3\text{S}_4$ ($x = 0.33$). It can be understood that the density of states (DOS) of the majority spins in $\text{Rb}_2\text{CoNi}_2\text{S}_4$ has no states around the Fermi level, whereas the DOS of the minority spins has states around the Fermi level. Therefore, this system is expected to behave as half metal. In addition, bands

immediately below the Fermi level in the majority spins and bands across the Fermi level in the minority spins are mainly consist of Ni 3d and Co 3d bands. In particular, the bands around the Fermi level in the minority spins are mainly consist of Co 3d bands. Therefore, this filling controlled system is expected to behave as ferromagnetism which is mainly derived from Co 3d spin.

In order to induce ferromagnetism in $\text{Rb}_2\text{Ni}_3\text{S}_4$, we also attempted partial substitution of Co^{2+} for Ni^{2+} experimentally.

Figure 6 shows the magnetic susceptibility as a function of temperature in specimens slightly doped with Co^{2+} . As shown, magnetism emerges paramagnetically and the magnetic susceptibility obeys the Curie law: $\chi(T) = \alpha + C/T$, where α is a constant including the diamagnetic susceptibility and C is the Curie constant represented by $C = N \mu_B^2 p_{\text{eff}}^2 / 3k_B [(p_{\text{eff}}^2 = g^2/S(S+1))]$. Therefore, the doped Co^{2+} s behave like magnetic ions with localized moments, where the amount of them marked in figure 6 was estimated by fitting the observed $\chi(T)$ to the above $\chi(T)$, assuming Co^{2+} to be in a low spin state (g value and S are assumed to be 2 and 1/2, respectively). The field dependence of magnetization $M(H)$ for specimens at 4 K are shown in figure 7, where the letters (A), (B), and (C) correspond to those in figure 6. Fittings to the Brillouin function: $M(H) = Np_b \mu_B B_S(H)$ ($p_b = gS$), were done to estimate the effective magnitude of p_b for the doped Co^{2+} . The obtained data on p_b for (A), (B), and (C) are 0.84, 0.86, and 0.74, respectively. Since these values can confirm the low spin state Co^{2+} , but are rather smaller than the nominal value of 1, some reductions in the magnitude of the spin

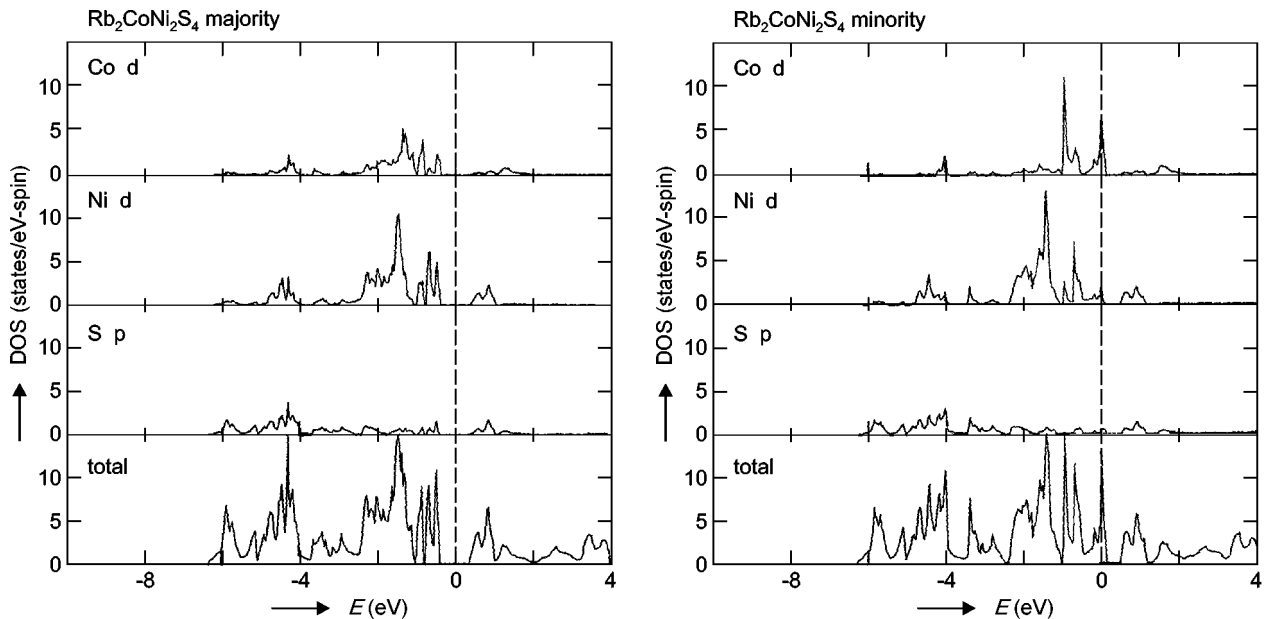


Figure 5. The density of states (DOS) of $\text{Rb}_2\text{CoNi}_2\text{S}_4$. Energy is measured from the Fermi level denoted by the vertical broken line.

moment may occur due to a possible enhancement of the antiferromagnetic spin correlation at low temperatures. Within these doping rates, we could not observe any residual moments which indicate the presence of ferromagnetic moments.

We also measured electric resistivity for the Co-doped samples in order to attempt to find the presence of metallic phase. In figure 8, the semilogarithmic plot of the temperature dependence of the specific resistivity $\rho(T)$ of 4 % Co-doped sample is shown for these parallel ($\rho \parallel$) and perpendicular ($\rho \perp$) to the b axis. As can be seen in figure 8, both $\rho \parallel$ and $\rho \perp$ data show the same behavior as a semiconductor with an activation energy of 0.4 eV in the range above room temperature. Since the gross feature is characteristic of a typical extrinsic semiconductor, the conductivity in the region below room temperature has an extrinsic origin, which is probably ascribed to a defect state due to the presence of faults in sulfur or rubidium. The activation energy in the region above room temperature is accordingly attributed to an intrinsic origin. The observed anisotropy in ρ , where $\rho \parallel$ is larger than $\rho \perp$, may reflect the two-dimensional characteristic of the crystal. In this Co-doping ratio of 4 %, we could not observe half metallic behavior that was predicted according to the LSDA band structure calculation.

CONCLUSIONS

The influence of water on magnetic behavior in single crystals grown by the flux method was studied for $Rb_2Ni_3S_4$. Specimens immersed into water showed ferromagnetic behavior, a residual magnetic moments of which grow with the increase of immersion time. The

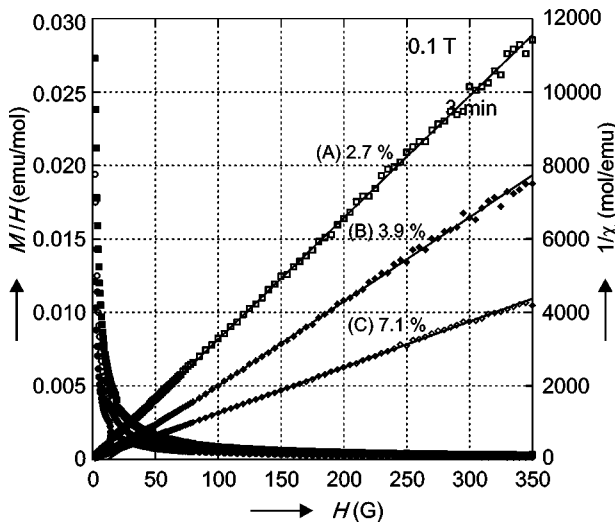


Figure 6. The M/H vs. T curve of Co^{2+} doped samples, where a field of 0.1 T is applied.

influence of Co-doping on $Rb_2Ni_3S_4$ was also studied in terms of the local spin density approximation (LSDA) band structure calculation together with the Co^{2+} doping experiments. The calculation showed that the Co substitution for Ni allows deriving novel ferromagnetic behavior of the half metallic ferromagnetism. However, the experimental results of Co^{2+} doped samples up to 7% showed that the partially substituted systems still remain to have localized paramagnetic and semiconductive features.

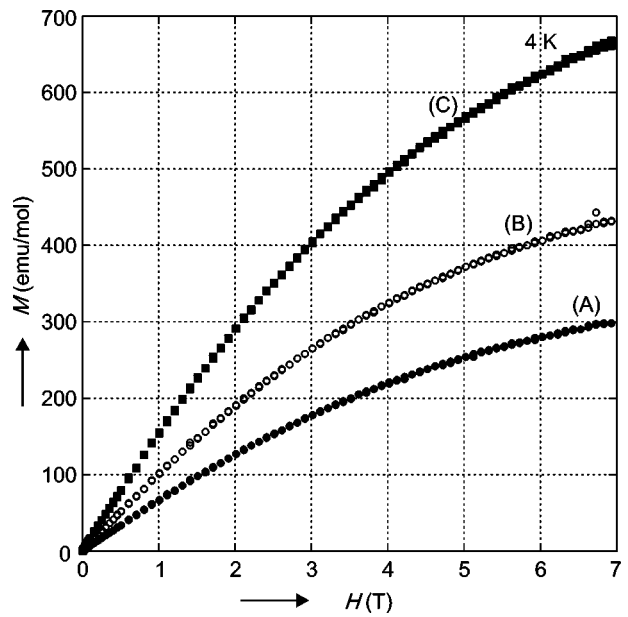


Figure 7. The M vs. H curve of Co-doped samples at 4 K.

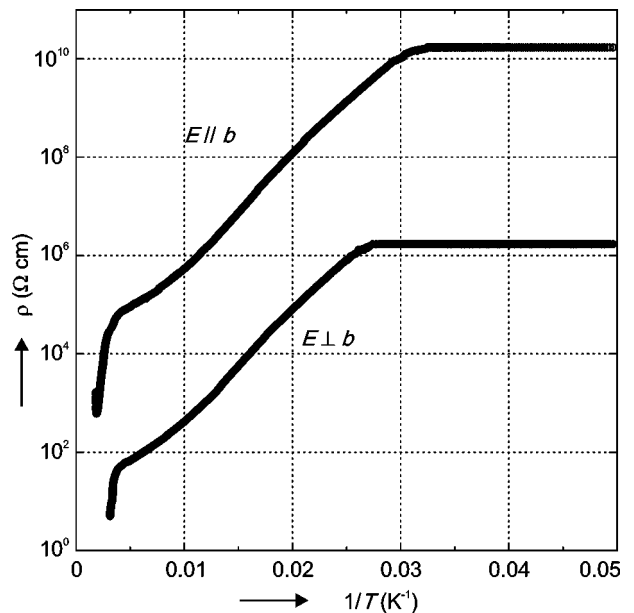


Figure 8. The $\log \rho$ vs. $1/T$ curve of a Co-doped sample.

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FERROMAGNETISMUS $\text{Rb}_2\text{Ni}_3\text{S}_4$ VYVOLANÝ
HYDRATACÍ A SUBSTITUCÍ KOBALTEM

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Studovali jsme vliv hydratace na magnetické chování monokrystalů $\text{Rb}_2\text{Ni}_3\text{S}_4$ vypěstovaných z taveniny, které jsou ze své podstaty nemagnetické, protože obsahuje nízkospinový Ni^{2+} v mřížce kagome. Vliv dopování $\text{Rb}_2\text{Ni}_3\text{S}_4$ kobaltem jsme studovali rovněž pomocí kvantově chemických výpočtů pásové struktury v aproximaci lokální spinové hustoty (LSDA). Zbytkové magnetické momenty jsme zjistili ve vzorcích po jejich ponoření do vody v závislosti na době ponoření. Výpočet pásové struktury LSDA naznačuje, že záměna Co za Ni umožňuje vznik nového magnetického ferromagnetického chování.