Crystal growth and characterization of Haldane chain compound Ni(C₃H₁₀N₂)₂NO₂ClO₄

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Abstract

The bulk single crystals of S = 1 chain compound Ni(C₃H₁₀N₂)₂NO₂ClO₄ are grown by using a slow evaporation method at a constant temperature and a slow cooling method. It is found that the optimum condition of growing large crystals is via slow evaporation at 25 °C using 0.015 mol Ni(ClO₄)₂·6H₂O, 0.015 mol NaNO₂, and 0.03 mol 1,3-propanediamine liquid dissolved into 30 ml aqueous solvent. High-quality crystals with size up to 18 × 7.5 × 5 mm³ are obtained. The single crystals are characterized by measurements of x-ray diffraction, magnetic susceptibility, specific heat and thermal conductivity. The susceptibilities along three crystallographic axes are found to exhibit broad peaks at ~ 55 K, and then decrease abruptly to zero at lower temperatures, which is characteristic of a Haldane chain system. The specific heat and the thermal conductivity along the c axis can be attributed to the simple phononic contribution and are analyzed using the Debye approximation.

Keywords:
A1. X-ray diffraction, A1. Solvents, A2. Growth temperature, B2. Magnetic materials

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Preprint submitted to Journal of Crystal Growth November 13, 2013
1. Introduction

During the past decades, one-dimensional quantum magnets have attracted an increasing interest because of Haldane’s well-known prediction that for the integer-spin chain system the ground state is separated from the first excited state by a gap (so-called Haldane gap), while for the half-integer spin system the excitation spectrum has no gap [1, 2, 3, 4, 5, 6, 7]. The existence of Haldane gap has a great impact on the low-temperature magnetic properties and has been verified in lots of one-dimensional quantum systems, such as $S=1$ Heisenberg chain compounds CsNiCl$_3$ [8, 9] and Ni(C$_2$H$_5$N$_2$)$_2$NO$_2$(ClO$_4$) [10], and $S=2$ quasi-linear chain compound Mn(2, 2'-bipyridine)Cl$_3$ [11, 12].

Nickel propylene-diamine nitrite perchlorate, Ni(C$_3$H$_{10}$N$_2$)$_2$NO$_2$ClO$_4$ (NINO), has been found to be an ideal Haldane chain system for its relatively weak interchain interaction and obvious magnetic anisotropy [13]. The crystal structure of single crystal NINO was first reported by Renard et al. [13]. In NINO, the $S=1$ spins of Ni$^{2+}$ are coupled along the $b$ axis with exchange interaction $J \approx -50$ K [14, 15]. Susceptibility measurement did not show long-range magnetic order down to 0.5 K, which indicates a negligible interchain exchange [13]. The Haldane gap, uniaxial anisotropy, and orthorhombic anisotropy parameters were identified as $E_g = 14.2$ K, $D = -11.5$ K, and $E = 2.1$ K, respectively [14]. Due to the role of crystalline field in NINO, the energy gap is actually split into three gaps with the values of $\Delta E_1 = 8.3$ K, $\Delta E_2 = 12.5$ K, and $\Delta E_3 = 21.9$ K [14]. When an external magnetic field is applied along the $a$ axis, $\Delta E_2$ keeps constant, $\Delta E_3$ increases, and $\Delta E_1$ decreases with increasing field, respectively. However, due to the existence of staggered transverse field, $\Delta E_1$ actually descends to a finite value at a critical field $B_c$, and then increases above $B_c$ [16, 17].

The growth of crystals from aqueous solution is a common method to synthesize organic single crystals [18, 19, 20]. The single crystals of NINO were synthesized by several groups via a slow evaporation method [13, 14, 16, 21]. However, the condition of crystal growth and the sizes of crystals were not depicted in their papers. Therefore, it is still necessary to make a detailed investigation on the conditions of crystal growth for NINO. In this
work, we try to grow NINO single crystals by using both a slow evaporation and a slow cooling method from the aqueous solution. It is found that the appropriate condition of growing NINO crystals is to dissolve 0.015 molar Ni(ClO$_4$)$_2$·6H$_2$O and NaNO$_2$ into 30 ml aqueous solvent with 0.03 mol 1,3-propanediamine and keep the solution at 25°C for a slow evaporation. The quality of obtained single crystals is characterized by the x-ray diffraction, and their physical properties are characterized by the magnetic susceptibility, specific heat, and thermal conductivity measurements.

2. Experimental details

2.1. Synthesis and crystal growth

Ni(C$_3$H$_{10}$N$_2$)$_2$NO$_2$ClO$_4$ is synthesized using Ni(ClO$_4$)$_2$·6H$_2$O, 1,3-propanediamine, and NaNO$_2$ as raw materials which are mixed with a stoichiometric ratio 1:1:2 in the aqueous solvent. The chemical reaction equation is

Ni(ClO$_4$)$_2$·6H$_2$O + NaNO$_2$ + 2C$_3$H$_{10}$N$_2$ → Ni(C$_3$H$_{10}$N$_2$)$_2$NO$_2$ClO$_4$ + NaClO$_4$ + 6H$_2$O.

2.5 ml liquid of 1,3-propanediamine (0.03 molar) is firstly mixed into the deionized water uniformly. Then 0.015 molar Ni(ClO$_4$)$_2$·6H$_2$O and 0.015 molar NaNO$_2$ are added to the solution slowly with stirring, and the reaction process occurs immediately, accompanied with releasing heat. The prepared solution is used to grow single crystals under several different conditions.

First, we investigate the influence of different degrees of the initial super-saturation of the solutions on the crystal growth at a constant temperature 25 °C. The pre-prepared tiny crystals are dropped into the solutions and act as seeds. The shapes and sizes of the crystals grown using different amounts of solvent are shown in Fig. 1. It is clear that the effect of the initial concentration of solution is remarkable on the crystallization of NINO. The detailed initial conditions at 25 °C, growth durations, and sizes of as-grown single crystals are listed in table 1. It is found that in the 20 ml aqueous solvent, the mahogany as-grown crystals have a typical dimension of (3.5–6.5) × (3.5–4.5) × (1.5–2.5) mm$^3$. From 30 ml aqueous solvent, we obtain very large single crystals with size up to (16–18) × (7.5–8) ×
and excellent crystallographic surfaces, as shown in Fig. 1(b). However, when the volume of solvent is larger than 30 ml, the sizes of as-grown crystals become smaller with gradually increasing the amount of solvent. It is known that the crystal growth from an aqueous solution is based on the existence of metastable supersaturation regions where spontaneous nucleation is impossible, so it is possible to grow a big single crystal from a seed [22]. For the current case, the degree of the initial super-saturation decreases with increasing the amounts of solvent under the condition that the amount of raw material is invariant at the given temperature 25 °C. It is likely that the concentration of the solution with 30 ml aqueous solution is just under or close to the metastable state making the crystallization occur continuously on seed crystals. Although increasing the super-saturation can accelerate the crystal growth, at a high super-saturation degree there is a strong tendency for crystals to nucleate spontaneously, i.e., to produce many small crystals at the same time rather than to form a single large one.

Based on the above results, we further investigate the influence of the temperature on the crystal growth in 30 ml aqueous solvent with the same amount of raw materials as the above. The morphological features of the obtained crystals are shown in Fig. 2. The detailed temperature conditions, growth periods, and sizes of as-grown single crystals are listed in Table 2. It turns out that when the temperature of the solution is above 60 °C, only a large amount of polycrystals are obtained and no sizeable single crystals can be formed. When the solution is kept at 35 °C, large single crystals with the typical size of (13.5–15) × (4–4.5) × (3.0–4.0) mm³ and bright surfaces are obtained. The sizes of single crystals become smaller with increasing temperature, as shown in Fig. 2. The reason can be as following: the solubility of NINO in the aqueous solvent increases as the temperature increases, which thus decreases the degree of super-saturation; on the other hand, increasing temperature enforces the driving force of the liquid-to-solid phase transition and thus accelerates the process of the crystal growth by enhancing the diffusions of the ions to the surface. However, a higher temperature simultaneously increases the energy diffusion of ions, and too high temperature makes diffusion too fast to form single crystals, just as the case of 60 °C growth indicates [20, 23].
In addition, a slow cooling method is also carried out to grow NINO single crystals. The slow cooling process of solvent with 30 ml deionized water is performed from 65 to 25 °C at a rate of 5 °C per day. The results are shown in Fig. 3. It can be seen that although single crystals as large as 11 × 5 × 3.5 mm³ can be formed, they have no regular shapes and clean cleavage planes, indicating that the present condition is not the most appropriate for the crystal growth of NINO. Actually, the slow cooling method is a much more proper way to grow those single crystals that have large temperature coefficients of solubilities, which also needs well-controlled temperature descending-rate.

To sum up, we compare the results of single crystal growth of NINO under different conditions, including both a slow evaporation method and a slow cooling method. It turns out that the slow evaporation at 25 °C in the 30 ml aqueous solvent with the solutes of 0.015 mol Ni(ClO_4)_2·6H_2O and 0.015 mol NaNO_2 as well as 0.03 mol 1,3-propanediamine is the most appropriate condition to grow the high-quality NINO single crystals. In passing, it is notable that compared with the growth of (CH_3)_2NH_2CuCl_3 (MCCL for short) single crystals using the slow evaporation method [20], the growth of NINO crystals shows some similar features with MCCL; for example, the sizes of crystals are greatly affected by the initial concentrations of the solutions, and it is difficult to get single crystals in the solutions at too high temperature.

2.2. Characterization

Powder x-ray diffraction measurements are carried out using an X’Pert PRO X-Ray diffractometer (PANalytical Company). Magnetization measurement is performed in the temperature range of 2 – 300 K in an applied field of 1 T using a commercial SQUID-VSM (Quantum Design) and specific heat is measured using a PPMS equipped with a ³He refrigerator (Quantum Design). The thermal conductivity with heat flow along the c axis (κ_c) is measured using a conventional steady-state technique. The data of κ_c at 4 – 100 K are obtained using a pulsed-tube refrigerator and the low-T data at 0.3 – 8 K are taken using a ³He refrigerator, with the temperature gradient detected by using a Chromel-Constantan thermocouple and two RuO_2 chip resistors, respectively [24, 25].
3. Results and discussion

3.1. X-ray diffraction

Figure 4 shows the result of x-ray powder diffraction at room temperature, in which the indices of diffraction peaks are determined according to the orthorhombic structure (space group \( Pbn2_1 \)) with lattice parameters \( a = 15.384 \) Å, \( b = 10.590 \) Å and \( c = 8.507 \) Å [13]. We also use the x-ray diffraction to determine the crystallographic axes and the results clearly indicate that the as-grown crystals are grown along the \( c \) axis and the largest cleavage surface of crystals is the \((100) \) plane, which coincide with the earlier results [14]. The rocking curve of the \((200) \) reflection is shown in Fig. 5(a), and the full width at half maximum (FWHM) is only 0.075\(^\circ\), indicative of the high quality of the single crystal. Figure 5(b) shows the \((h00) \) diffraction pattern of this crystal.

3.2. Magnetic susceptibility and magnetization

Figure 6(a) shows the temperature dependences of magnetic susceptibilities in 1 T field applied along three crystallographic axes \( a, b, \) and \( c, \) respectively, which are essentially consistent with the previous measurement [14]. It is clearly seen that three magnetic susceptibilities exhibit rounded peaks at \( \sim 55 \) K, and fall down abruptly to zero at lower temperatures, which reflects the excitation gap of NINO and is characteristic of the Haldane chain. Note that the effect of the crystalline field is remarkable only at very low temperatures. It is applicable to employ the theoretical calculation for an isotropic Heisenberg chain by the exact diagonalization at relatively high temperature, which is given by [26]

\[
\chi = \frac{N g^2 \mu_B^2}{k_B T} \left[ \frac{2 + 0.01947x + 0.777x^2}{3 + 4.346x + 3.232x^2 + 5.834x^3} \right],
\]

where \( \chi \) is the molar susceptibility, \( x = |J|/k_B T, \) \( N \) the number of Ni\(^{2+} \) ions per mole NINO, \( g \) the Landé factor, \( \mu_B \) the Bohr magneton, and \( k_B \) the Boltzmann constant. As shown in Fig. 6(a), the data at high temperature between 50 and 300 K are well fitted using the above equation, with the parameters \( J = -50.0 \) K, \( g_a = 2.42, \) \( g_b = 2.25, \) and \( g_c = 2.37. \) The fitting parameters are found to be in good consistent with those in some former works [26].
The magnetization curves of NINO along three principal axes $a$, $b$, and $c$ at $T = 2$ K are shown in Fig. 6(b). It is observed that the magnetization process shows an obvious anisotropic behavior along three different crystallographic axes. The magnetization along the $a$ axis shows a slightly faster slope than that along the $c$ axis, and in contrast the magnetization of the $b$ axis exhibits a rather steep increase with increasing magnetic field. In spite of these obvious distinctions, a noticeable feature of the $M(H)$ curves is that the magnetization is in fact rather small. The reason is obvious, that is, at low temperatures the system is nonmagnetic because of the presence of the Haldane gap [27]. Only when an applied field quenches the energy gap, the system becomes magnetic. Actually, for NINO the magnetic field needed to close the gap is rather high, about 9 T [14].

3.3. Specific heat and thermal conductivity

Figure 7(a) shows the specific heat at low temperatures, which do not show any sign of phase transition. To quantitatively analyze the data, we use the simple Debye approximation of the phonon specific heat [28]

$$C_p = \beta T^3 + \gamma T^5 + \delta T^7,$$

where $\beta = (12\pi^4 nk_B/5\Theta_D^3)$ with $n$ the number density of the atoms in NINO and $\Theta_D$ the Debye temperature; $\gamma$ and $\delta$ are temperature-independent coefficients. Note that the high-power terms are included because at not very low temperatures the density of phonon modes of a solid actually deviates from the $\omega^2$-law of Debye’s presupposition. Figure 7(a) shows that the experimental data can be well fitted to Eq. (2), indicating that the contribution of the specific heat is completely due to the lattice vibration. The corresponding fitting parameters are $\beta = 5.74 \times 10^{-3}$ J/K$^4$ mol, $\gamma = -1.24 \times 10^{-5}$ J/K$^6$ mol, and $\delta = 1.17 \times 10^{-8}$ J/K$^8$ mol. The Debye temperature $\Theta_D = 236.4$ K is calculated using the fitting parameter $\beta$.

Figure 7(b) shows the temperature dependence of the thermal conductivity along the $c$ axis of a crystal with size of $3.7 \times 0.6 \times 0.4$ mm$^3$. It is seen that a pronounced phononic peak is observed at about 6 K. Here we analyze $\kappa_c$ using the Debye approximation for the
phonon spectrum and relaxation approximation, where the phonon thermal conductivity is expressed as

\[ \kappa_{ph} = \frac{k_B}{2\pi^2 v} \left( \frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau(\omega, T) dx, \]  

in which \( x = \hbar \omega / k_B T \) is dimensionless, \( \omega \) is the phonon frequency, and \( 1/\tau(\omega, T) \) is the phonon-scattering relaxation rate. The average sound velocity \( v = 1644 \) m/s is calculated from the Debye temperature using the formula \( \Theta_D = v(h/k_B)(6\pi^2 n)^{1/3} \). The relaxation time takes three terms as follows

\[ \tau^{-1} = v/L + A\omega^4 + B T \omega^3 \exp(-\Theta_D/b T), \]

which represent the phonon scattering by the grain-boundary, point-defect, and phonon-phonon Umklapp scattering, respectively, with \( L, A, B \) and \( b \) free parameters. The thermal conductivity can be well fitted to Eq. (1) up to 70 K, as shown in Fig. 7(b). The fitting parameters are \( L = 7.1 \times 10^{-5} \) m, \( A = 2.0 \times 10^{-41} \) s\(^3\), \( B = 9.6 \times 10^{-29} \) K\(^{-1}\) s\(^2\), and \( b = 10.2 \). These indicates that although NINO is a magnetic insulator, the magnetic excitations make no contribution to \( \kappa_c \) because the heat current is perpendicular to the spin-chain direction.

4. CONCLUSIONS

Different growth conditions for a slow evaporation method and a slow cooling method are used to grow NINO single crystals. It is found that the optimum condition of growing large single crystals is via the slow evaporation at constant temperature of 25 \(^\circ\)C using the raw materials (0.015 mol Ni(ClO\(_4\))\(_2\)·6H\(_2\)O, 0.015 mol NaNO\(_2\), and 0.03 mol 1,3-propanediamine liquid) dissolved into 30 ml aqueous solvent. X-ray diffraction data have confirmed the good crystallinity of the grown crystals. The magnetic susceptibilities are found to show broad maximum at about 55 K, which is characteristics of the 1D Haldane chain system, and the higher-\( T \) data of \( \chi \) are analyzed with the isotropic Heisenberg model. The low-temperature specific heat and the \( c \)-axis thermal conductivity are found to be purely phononic behaviors and can be well described by the Debye model.
ACKNOWLEDGMENTS

This work was supported by the Chinese Academy of Sciences, the National Natural Science Foundation of China, and the National Basic Research Program of China (Grant Nos. 2009CB929502 and 2011CBA00111).

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Figure 1: NINO single crystals grown from different amounts of aqueous solvents at 25 °C. Photos (a), (b), (c), and (d) correspond to the 20, 30, 40, and 50 ml aqueous solvent, respectively.
Figure 2: NINO single crystals grown from the 30 ml solvents at the temperatures of 35, 45, and 55 °C, respectively.
Figure 3: NINO single crystals grown from 30 ml solvent with temperature decreasing slowly from 65 to 25 °C at a rate of 5 °C per day.
Figure 4: X-ray powder diffraction pattern of NINO at room temperature.
Figure 5: (a) X-ray rocking curve of the (200) reflection, with a FWHM of only 0.075°. (b) (h00) diffraction pattern.
Figure 6: (a) Temperature dependences of magnetic susceptibilities in 1 T field applied along three crystallographic axes $a$, $b$, and $c$, respectively. The solid lines show the theoretical fitting curves in the temperature range between 50 and 300 K (see text). (b) Magnetic-field dependence of magnetization at $T = 2$ K.
Figure 7: (a) Low-temperature specific heat of NINO single crystal. The solid line represents the theoretical fitting curve (see text). (b) Temperature dependence of thermal conductivity with heat current along the $c$ axis. The solid line represents the fitting curve based on the Debye model for the phononic heat transport (see text).
Table 1: Results for different volumes of aqueous solution kept at 25 °C. The raw materials are 0.015 mol Ni(ClO$_4$)$_2$·6H$_2$O and 0.015 mol NaNO$_2$ as well as 0.03 mol 1,3-propanediamine.

| Volume (ml) | Growth Period (days) | Crystal State |
|-------------|----------------------|---------------|
| 20          | 34                   | big crystals, size about (3.5–6.5)×(3.5–4.5)×(1.5–2.5) mm$^3$ |
| 30          | 58                   | large bright crystals, size about (16–18)×(7.5–8)×(3.5–5) mm$^3$ |
| 40          | 62                   | small crystals, size about (3.5–4.5)×(1–2)×(0.2–0.4) mm$^3$ |
| 50          | 65                   | small thin pieces, size about (2.0–3)×(1.2–2.2) mm$^2$ |
Table 2: Results for different growing temperatures in 30 ml aqueous solution. The raw materials are 0.015 mol Ni(ClO$_4$)$_2$·6H$_2$O and 0.015 mol NaNO$_2$ as well as 0.03 mol 1,3-propanediamine.

| Temperature ($^\circ$C) | Growth Period (days) | Crystal State                                      |
|-------------------------|----------------------|---------------------------------------------------|
| 35                      | 32                   | large bright crystals, size about (13.5–15)×(4–4.5)×(3.0–4.0) mm$^3$ |
| 45                      | 20                   | big bright crystals, size about (6.5–9)×(2–3)×2.5 mm$^3$  |
| 55                      | 7                    | small irregular crystals                          |
| 60                      | 5                    | none                                              |