Specific Heat on Single-crystalline YVO₃

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Abstract
The specific heat of single-crystalline YVO₃ was measured from 2 K up to 250 K at zero field. The results reveal three transitions, at around 75, 115, and 200 K. The transitions at around 115 K and 200 K show that the phase transition is of the second-order type, whereas at around 75 K, unusual features of the specific heat are found. These unusual features are attributed to the effect of a large change in the volume. The specific heat data were analyzed in terms of a lattice contribution, a Schottky contribution and an excess magnetic contribution at high temperature. The contribution well above the magnetic ordering temperature is ascribed to short-range interactions due to the presence of strong magnetocrystalline anisotropy. The magnetic entropy can be obtained by using this approach is 9.13 J/mole K which is close to the theoretical estimate for the S=1 system.

1. Introduction
The RVO₃ compounds (with R is rare earth element) have become an interesting series of compounds since the discovery of an anomalous diamagnetism in LaVO₃. The anomalous diamagnetism occurs when the magnetization reverses its direction with respect to the applied magnetic field below the antiferromagnetic ordering. In contrast to a previous study on polycrystalline material [1], single-crystalline YVO₃ has shown a sign reversal magnetization [2]. Sign reversals of the magnetization occur at around 95 K and 77 K. These temperatures will be denoted as T₁ and T₂, respectively. Both temperatures are below the long-range canted antiferromagnetic ordering temperature Tₘ ≈ 116 K. In this compound, the sign reversal of the magnetization is observed both in ZFC and in FC samples. Another remarkable transition in single crystalline YVO₃ is found at 200 K. This salient transition in the magnetic susceptibility occurs as a change in the Curie-Weiss slope resulting in a change of the effective moment from 2.81 µₑ below 200 K to 2.31 µₑ below 200 K [3]. A structural phase transition at that temperature has also been observed in X-ray as well as in neutron powder diffraction studies. Recently, a forbidden reflection in the Pbnm symmetry has been found below 200 K in synchrotron X-ray single crystal diffraction [4] and in optical studies showing a lowering of the symmetry [5].

This report is a detailed description of the specific heat result reported in Ref. 4. The specific heat data of the single-crystalline sample, which are different from the data for a polycrystalline sample [6], will be presented. We obtain a consistent magnetic entropy for S = 1 using Schottky analysis. This method might be applied to obtain the magnetic contribution to the specific heat in transition metal oxide compounds.

2. Experimental Methods
The specific heat of single-crystalline YVO₃ was measured at constant pressure by using two different experimental systems and two different samples. The samples, typically rectangular, with the weight of 158.34 mg and 50.33 mg, were labeled as sample A and sample B, respectively. Sample A was measured by using a semiadiabatic method in a home-made specific heat equipment [6]. In this setup, the measurement can only be run automatically during warming up the sample. Unfortunately, it is found that upon heating above 75 K, the heat contact between the sample and the holder was lost. Having this constraint, the measurement was performed only in the temperature range from 100 to 250 K. The other sample, sample B, was measured by using a relaxation method in a commercial Quantum Design PPMS. This apparatus can be run automatically with heating and cooling mode. In this setup, the experiment was performed in the temperature range from 2 K to 250 K. In order to refine the data at low temperature below 100 K, the experiments were repeated several times above and below 75 K. A reasonably good thermal contact between the sample and the holder can be achieved by a rapid quenching or warming across the transition temperature at around 75 K.

3. Results and Discussion
The temperature dependence of the specific heat for single-crystalline YVO₃ is presented in Fig. 1. The data have been corrected for the addenda. Both sample A and sample B show a good reproducibility for the peaks at around 200 K T₁ and 115 K, T₂. A polycrystalline sample, aside from the magnetic transition, Tₘ, at 116 K, Borukhovich et al. had observed only the transition at 77 K, T₆ [7]. In contrast to that, the single-crystalline specific heat data clearly reveal three transitions. Two transitions, at T₁ and T₂, are in agreement with the previous measurements of the magnetization and the crystallographic structure. These results confirm that both transitions are of the second-order type. A discrepancy, however, is found for the transition at T₆ around 75 K. A first-order transition observed as a discontinuation in the magnetization as well as in lattice parameters at T₆ is not corroborated by the appearance of a sharp peak in the specific heat measurement. Instead, a jump in the specific heat is found, which indicates that the transition is of a second-order type. This discrepancy might be attributed to the inappropriate temperature step in measurement compared with the width of the transition. It is known that at T₆, the a axis and c axis increase by around 1% and 2%, respectively, while the b axis decreases by about 3%. Overall, this gives rise to a volume compression of about 1% [4]. In the series of measurements, the heat contact between the sample and the holder becomes worse at lowering the temperature, or it can totally be lost at increasing temperature while passing T₆. This effect may arise from less accuracy of the measurement around the transition. It is also found that the sample can even be broken by clamping the sample to the holder. In order to be able to obtain more information around the first-order transition, a powder measurement is suggested. In the powder sample, it is expected that there will be more degree of freedom in releasing the strain force, as shown in Ref. 4.
Fig. 1. The temperature dependence of the specific heat of the single-crystalline YVO$_3$ from 2 to 250 K. Sample B and sample A are plotted by the ◊ and • symbol, respectively. The inset figure is the specific heat jump at around 75 K with a thermal hysteresis of about 0.9 K.

The temperature dependence of the specific heat is analyzed in terms of the lattice contribution, $C_{lat}$, the electronic Schottky contribution, $C_{sch}$, and the excess specific heat, $\Delta C$, as shown in Eq. 1:

$$C(T) = C_{lat}(T) + C_{sch}(T) + \Delta C(T).$$

As a first approximation, the lattice contribution at low temperature is described by the Debye approximation, $C_{lat} = \frac{\alpha}{3} T^3$. The coefficient $\alpha$ is determined from the slope in the $C/T^2$ vs $T$ plot. It is found that the curve starts to deviate from the linear dependence above 40 K. The Debye temperature of 460 K is obtained by fitting the data below 40 K using a Debye function. It is obvious that above 40 K, the $C_{lat}$ starts to overwhelm the experimental data. This indicates that the Debye approximation, which considers only the acoustic mode of the phonons, is insufficient to describe the lattice specific heat. In order to have a better description for the lattice contribution, the optical mode has to be included. The contribution of the optical mode can be considered by using an Einstein function. The $C_{lat}$ is, therefore, expressed in a hybrid Debye-Einstein model [8], as shown in Eq. 2:

$$C_{lat}(T) = \frac{\alpha D(\theta_D/T)}{\theta_D} + \frac{\alpha E(\theta_E/T)}{\theta_E}$$

where $D(\theta_D/T)$ and $E(\theta_E/T)$ are Debye and Einstein functions, respectively. The Debye temperature, $\theta_D$, is fixed at 460 K, while the Einstein temperature, $\theta_E$, of 800 K is adopted from one of the oscillators used in the YMnO$_3$ compound [9]. The coefficient $\alpha_D$ of 2/3 and $\alpha_E$ of 1/3 are obtained by extrapolating the low-temperature data to the high-temperature data. The result of this extrapolation is shown in Fig. 2.

Another important contribution to the specific heat data is given by the electronic Schottky term. It is mentioned earlier that the low energy levels of YVO$_3$ consist of a singlet ground state and a doublet excited state. This scheme can be described by a two-level Schottky contribution as presented in Eq. 3:

$$C_{sch} = R \left( \frac{\Delta}{\theta_s} \right)^2 \frac{\exp(\Delta/T)}{\left[ 1 + \exp(\Delta/T) \right]^2}$$

with $g_0$ and $g_1$ are the degeneracies of the ground state and the excited state, respectively. $\Delta$ is the energy separation between the two levels. The ratio $g_0/g_1$ and the energy separation, $\Delta$, are taken as free parameters to fit the data below 30 K and the data ranging from 75 to 80 K in the $C$ vs $T$ plot. The best fit is provided by the parameters $g_0/g_1 = 0.51$ and $\Delta = 196$ K. These parameters are in agreement with the theoretical prediction for the two-level state, with the energy separation of about 200 K. The result of this fitting is depicted in Fig. 2. It is interesting to note that the Schottky contribution from 30 to 75 K gives a smooth extrapolation curve in the total specific heat, as shown in Fig. 2. The smooth extrapolation points below the magnetic transition turn out to be a bump in the $C/T$ curve after subtracting the lattice contribution, as displayed in Fig. 3. A bump feature has recently been reported as well for the manganese oxides, i.e., for YMnO$_3$, LuMnO$_3$, and ScMnO$_3$ [10]. The Schottky
Theoretical, the magnetic specific heat. The total entropy, obtained by numerical integration in this temperature range, is 2.88 J/mole K, and the average magnetic entropy obtained from the data 1 and data 2 is 8.38 J/mole K. This value is smaller compared to the theoretical estimation. The expected total magnetic entropy is given by the Schottky contribution, below 120 K, and the excess magnetic entropy obtained from the data 1 and data 2 is about the theoretical value. This demonstrates that the loss of entropy in data 1 is possibly due to the local effect in the electronic structure (reoccupation of the in-plane orbitals) at the first-order transition. This finding is compatible with the observed change of the orbital ordering and the Jahn-Teller distortion at the first order transition discussed earlier. This local effect might also be the reason for the small change of the magnetic entropy at the Ts as shown in Fig. 4(b).

Turning our attention to the transition at around 200 K, Ts, the peak in the specific heat data at this temperature confirms that the change in the crystallographic structure, from orthorhombic (Pbnm) to monoclinic (P2_1/a) with an a-type Jahn-Teller distortion, is of a second-order type. This transition was not observed in the specific heat measurement in a polycrystalline sample [7]. Besides a change in slope of the inverse magnetic susceptibility [3] and of the lattice parameters observed by the X-ray powder diffraction, which were observed previously, the recent synchrotron X-ray single crystal diffraction [4], as well as the infrared spectroscopy, are able to detect the lowering of Pbmn symmetry [5] at Ts. While the synchrotron X-ray detects an emergence of the forbidden reflection for Pbmn symmetry as lowering temperatures below Ts, the infrared spectroscopy detects new modes from the infrared active. An evidence for the orbital ordering in YVO_3 has recently been reported by means of the crystallographic studies [4] similar to those for the LaMnO_3 [11] and resonance inelastic X-ray scattering study [12]. The change in the crystallographic structure at Ts, as described earlier, has provided evidence of the onset of the orbital ordering.

Figure 5 shows the specific heat between 130 and 250 K after subtracting the lattice contribution, the Schottky contribution and the excess of the magnetic specific heat. The total entropy, obtained by numerical integration in this temperature range, is 2.44 J/mole K. Since there are three types of d orbitals involved under this consideration; therefore a rough estimate of the orbital entropy is given by R ln(3) = 9.13 J/mole K. The experimental value is too small in comparison to this estimate. This discrepancy should be a subject for further investigation, besides a comparison of the orbital entropy in the different perovskite system.
Fig. 5. The temperature dependence of the specific heat from 120 to 250 K after subtracting the $C_{\text{lat}}$, $C_{\text{coh}}$, and $\Delta C_{\text{m}}$. The continuous line is the entropy obtained from the specific heat at this temperature range.

4. Conclusions

We have presented the preparation of single-crystalline YVO$_3$ by using the TSFZ technique and its characterization. YVO$_3$ is unique among the transition metal oxides. It exhibits a peculiar interplay between the crystal structure, orbital ordering, and spin ordering. Besides a well-known second order metal antiferromagnetic transition at around 115 K, the result from the specific heat has established that there is a phase transition at 200 K with a nature of second order type. At around 75 K, $T_s$, the specific heat shows an unusual feature that cannot be described with a common expectation for the type of phase transition. Experimentally, the effects of the structural transition at 75 K are attributed to the uncertainty of the data around this transition. The amount of magnetic entropy which is analyzed by including the Schottky contribution shows a small loss of magnetic entropy. This loss is due to a local effect in the change of the electronic structure around $T_s$.

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References

[1] H. C. Nguyen and J. B. Goodenough, "Magnetic studies of some orthovanadates," Phys. Rev. B, vol. 52, no. 1, pp. 324–334, Jul. 1995, doi: 10.1103/PhysRevB.52.324.
[2] Y. Ren, T. T. M. Palstra, D. I. Khomskii, E. Pellegrin, A. A. Nugroho, A. A. Menovsky, and G. A. Sawatzky, "Temperature-induced magnetization reversal in a YVO$_3$ single crystal," Nature, vol. 396, no. 6710, pp. 441–444, Dec. 1998, doi: 10.1038/24802.
[3] Y. Ren, T. T. M. Palstra, D. I. Khomskii, A. A. Nugroho, A. A. Menovsky, and G. A. Sawatzky, "Magnetic properties of YVO$_3$ single crystals," Phys. Rev. B, vol. 62, no. 10, p. 6577, Sep. 2000, doi: 10.1103/PhysRevB.62.6577.
[4] G. R. Ilkate, T. T. M. Palstra, Y. Ren, A. A. Nugroho, and A. A. Menovsky, "Transition between orbital orderings in YVO$_3$," Phys. Rev. Lett., vol. 87, no. 24, p. 245501, Oct. 2001, doi: 10.1103/PhysRevLett.87.245501.
[5] A. A. Tsvetkov, F. F. Mena, Y. Ren, I. S. Elfimov, P. H. M. Van Loosdrecht, D. Van Der Marel, A. A. Nugroho, A. A. Menovsky, and Sawatzky, G. A., "Optical and magneto-optical study of orbital and spin ordering transitions in YVO$_3$", Physica B: Condensed Matter, vol. 312-313, pp. 783-784, Mar. 2002, doi: 10.1016/S0921-4526(01)01494-6.
[6] N. H. Kim-Nguy, "Magnetic Phase Transitions in NdMn$_2$ and Related Compounds," Universiteit van Amsterdam, 1993.
[7] A. S. Borukhovich, G. V. Bazuev, G. P. Shvikin, "Specific heat and magnetic phase in LaVO$_3$", Sov. Phys. Solid State, vol. 16, p. 191, 1974.
[8] B. F. Woodfield, J. L. Shapiro, R. Stevens, J. Boerio-Goates, and M. L. Wilson, "Critical phenomena at the antiferromagnetic transition in MnO", Phys. Rev. B, vol. 60, no. 10, pp. 7335–7340, Sep. 1999, doi: 10.1103/PhysRevB.60.7335.
[9] A. Muñoz, J. A. Alonso, M. J. Martinez-Lope, M. T. Casais, J. L. Martinez, and M. T. Fernández-Díaz, "Magnetic structure of hexagonal RMnO$_3$ (R = Y, Sc): Thermal evolution from neutron powder diffraction data," Phys. Rev. B, vol. 62, no. 14, pp. 9498–9510, Oct. 2000, doi: 10.1103/PhysRevB.62.9498.
[10] D. G. Tomuta, S. Ramakrishnan, G. J. Nieuwenhuys, and J. A. Mydosh, "The magnetic susceptibility, specific heat and dielectric constant of hexagonal YMnO$_3$, LaMnO$_3$ and ScMnO$_3"", J. Phys. Condens. Matter, vol. 13, no. 20, pp. 4543–4552, May 2001, doi: 10.1088/0953-8984/13/20/315.
[11] Rodriguez-Carvajal, M. Hemion, F. Mouta, A. H. Moudden, L. Pinsard, and A. Revcolevschi, "Neutron-diffraction study of the Jahn-Teller transition in stoichiometric LaMnO$_3$", Phys. Rev. B, vol. 57, no. 6, pp. R3189–R3192, Feb. 1998, doi: 10.1103/PhysRevB.57.R3189.
[12] E. Benckiser, L. Fels, G. Ghiringhelli, M. Moretti Sala, T. Schmitt, J. Schlappa, V. N. Strocov, N. Mufti, G. R. Blake, A. A. Nugroho, A.A. T. M. Palstra, M.W. Haverkort, K. Wohlräud, and M. Grüninger, "Orbital superexchange and crystal field simultaneously at play in YVO$_3$: Resonant inelastic x-ray scattering at the v L edge and the O K edge", Phys. Rev. B, vol. 68, pp. 205115, Nov. 2003, doi: 10.1103/PhysRevB.68.205115.