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Calorimetric Study on Metal-Insulator Transition of Quasi-One-Dimensional $BaVS_3$

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The specific heat of $BaVS_3$, which undergoes a metal-insulator transition at $T_{MI} = 70$ K, was measured in the temperature range of 1.4 K to 300 K. A specific heat anomaly was found at T_{MI}. The entropy change associated with this anomaly is estimated to be 4.7 J/K mol, which is close to $R \ln 2$, the expected magnetic entropy for $S = 1/2$ spins of V atoms. At low temperatures, a T-linear contribution of the specific heat with an apparent γ value of 15.7 mJ/K^2 mol was observed in spite of the absence of conduction electrons. This T-linear contribution may be attributed to spin wave excitations for a one-dimensional antiferromagnet.

KEYWORDS: quasi-one-dimensional antiferromagnet, $BaVS_3$, specific heat, magnetic entropy, spin wave, spin frustration, triangular lattice

Metal-insulator transition has recently attracted much attention in relation to the high-T_c superconductivity in copper oxides and the Kondo coherence gap formation in heavy fermion compounds, in which the strong electron correlation plays an important role. In many cases, metal-insulator transitions occur via complex mechanisms, accompanying magnetic and structural transitions. Consequently, they exhibit many complicated but interesting physical properties.

The quasi-one-dimensional sulfide $BaVS_3$, which has a hexagonal $P6_3/mmc$ structure above $T_S = 240$ K and an orthorhombic one below T_S, exhibits a metal-insulator transition at $T_{MI} = 70$ K accompanied by a sharp peak in the susceptibility.[1,2] The high-temperature metallic phase shows a poor conductivity ρ of 10^{-2} Ωcm. The susceptibility obeys the Curie-Weiss law above T_{MI} and has a minimum below T_{MI} at around $T_X = 30$ K. The magnetic properties in the insulating phase are intriguing. Below T_X, finite hyperfine fields were observed by both zero field NMR[3] and inelastic spin flip neutron scattering analysis.[4] In addition, other experimental findings indicate that a magnetic phase transition occurs at T_X. The intensity of elastic nuclear peaks of neutron diffraction decreases suddenly at T_X with decreasing temperature.[4] The linewidth of the nuclear spin echo spectrum and spin-spin relaxation rate $1/T_2$ of ^{51}V exhibit an anomaly at T_X.[3] These observations indicate that the onset of three-dimensional magnetic ordering occurs at T_X. However, no magnetic Bragg peak was detected in a precise neutron diffraction experiment performed at 5 K.[5] For the magnetic state in the intermediate temperature range, $T_X < T < T_{MI}$, Nishihara and Takano suggested a partial formation of a non-magnetic pairing of V atoms, based on their NMR measurement results,[3] although precise neutron diffraction analysis revealed no superlattice line to prove this pairing model.

In order to explain the origin of the metal-insulator transition and magnetic properties of $BaVS_3$, several models have been proposed, for example, spin-pairing,[3] Mott transition,[6] and Kondo insulator models.[7] However, none of them can be used to explain all experimental results consistently, and the physical properties of $BaVS_3$ are not comprehensively understood yet, although these anomalous physical properties seem to be caused by low dimensional characteristics of this compound. We report on the results of detailed specific heat measurements of $BaVS_3$ and discuss unsolved problems from a thermodynamical point of view. The specific heat of $BaTiS_3$, which has the same crystal structure as the high temperature phase of $BaVS_3$ over the entire temperature range, was also measured as a nonmagnetic reference material.

Polycrystalline samples were prepared by heating of a mixture of BaS, V (or Ti) and S in an evacuated quartz tube at 1223 K for 4 days. To avoid reaction of the mixture with the quartz tube, carbon crucibles were used. After the prepared samples were ground, they were heated again at 923 K with excess sulfur for 3 days to ensure stoichiometry. Without the last heat treatment, sulfur-deficient samples which show ferromagnetism at low temperatures were obtained. The results of powder X-ray diffraction analysis performed at room temperature confirmed that the samples are in a single phase of hexagonal $P6_3/mmc$ with lattice parameters $a = 6.697$ Å and $c = 5.612$ Å for $BaVS_3$, and $a = 6.743$ Å and $c = 5.832$ Å for $BaTiS_3$. Magnetic susceptibility was measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5 K to 300 K. The applied magnetic field was 10 kOe.

Specific heat measurements were performed in the temperature range of 1.4 K to 300 K by a standard adiabatic heat pulse method. Measurements were performed in two temperature ranges, 1.4 K to 35 K and 15 K to 300 K, using different apparatuses. For lower temperature measurements, powder samples were pressed

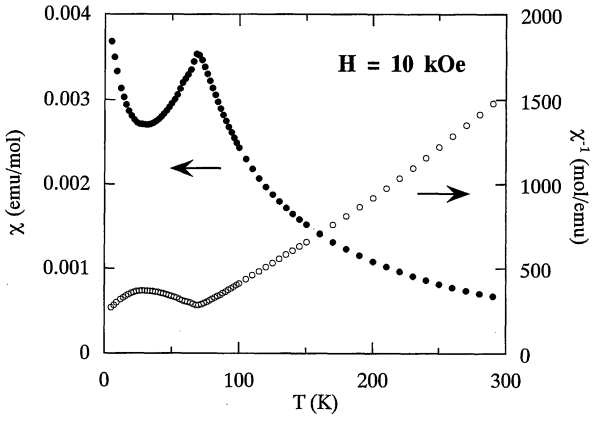

Fig. 1. Magnetic susceptibility (closed circles) and inverse susceptibility (open circles) of $BaVS_3$.

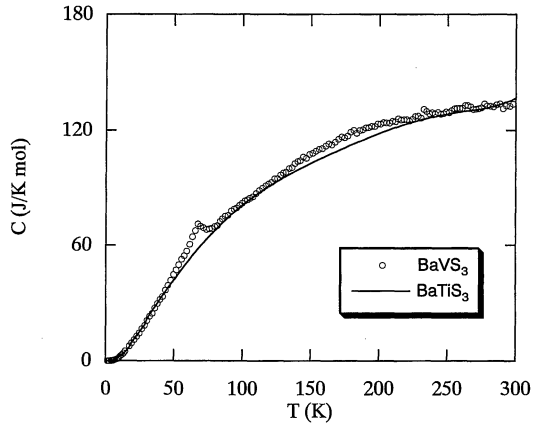

Fig. 2. Specific heat of $BaVS_3$ (open circles) and $BaTiS_3$ (solid curve, nonmagnetic reference).

into disk-shaped pellets with pure fine Cu powder as a binder and for thermal conduction. For higher temperature measurements, the powder samples were pressed within Cu tubes for the same purpose. The sample heat capacity fraction is from 25% to 82% of the total heat capacity. In the case of $BaTiS_3$, only the higher temperature measurements were performed.

The magnetic susceptibility of $BaVS_3$ is shown as a function of temperature in Fig. 1. A sharp peak was observed at $T_{MI} = 70$ K, and above 80 K, the magnetic susceptibility shows Curie-Weiss-like behavior. A minimum is visible at about $T_X = 35$ K. These features are consistent with previous reports.[2] However, we found that T_X depends on samples. It seems that T_X is determined by the sum of two components of susceptibility: the up-turn at low temperatures and the tail of the sharp peak at T_{MI}. Therefore, T_X as determined from the susceptibility may shift depending on the magnitude of the component which contributes to the up-turn of the susceptibility, whose origin is not obvious. The inverse susceptibility is given by open circles in Fig. 1. Above 250 K, the inverse susceptibility curve slightly deviates from the Curie-Weiss law. Therefore, the susceptibility was fitted to the Curie-Weiss law in the two temperature ranges 80 K $< T <$ 150 K and 150 K $< T <$ 300 K. The derived Weiss temperature, Θ, and effective moment, μ_{eff}, are $\Theta = 14.4$ K and $\mu_{eff} = 1.17\ \mu_B$/mol for 80 K $< T <$ 150 K, and $\Theta = 52.9$ K and $\mu_{eff} = 1.08\ \mu_B$/mol for 150 K $<$ T $<$ 300 K respectively, which are in good agreement with previous measurements.[6]

The specific heat of $BaVS_3$ in the entire temperature range of 1.4 K to 300 K is shown in Fig. 2. An anomaly is clearly found at around 70 K (T_{MI}) and no anomalies are detected at around 30 K (T_X) and 240 K (T_S). This indicates that T_X, which depends on samples, is not a magnetic transition point accompanying an entropy change associated with $S = 1/2$ of V atoms. The solid curve in the figure shows the specific heat of $BaTiS_3$, which we regard as the lattice specific heat, C_L, of $BaVS_3$. The result cannot be fitted to the Debye formula with a single Debye temperature but is well fitted to the model proposed for strongly anisotropic crystals.[8] The C_L below 15 K was extrapolated using this model. The extra specific heat (ΔC) was estimated by subtracting C_L from the observed values as plotted against T in Fig. 3. A sharp peak is found at around T_{MI} and an another broad maximum is visible at around 160 K. The anomaly around 160 K was also observed in other experiments such as ones on the susceptibility.[6]

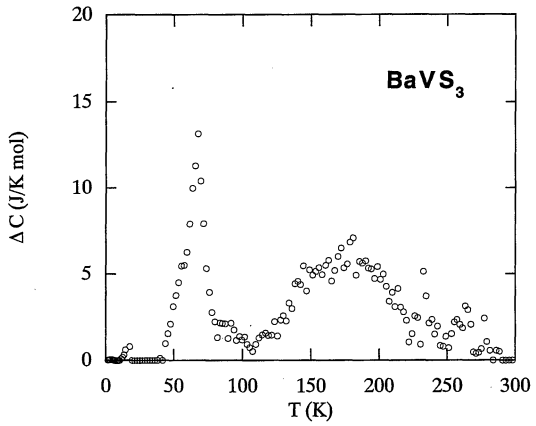

Fig. 3. Extra specific heat of $BaVS_3$, estimated by subtracting the specific heat of $BaTiS_3$ from the specific heat of $BaVS_3$.

The extra entropy is calculated as shown in Fig. 4. The horizontal lines in Fig. 4 are the expected magnetic entropy for the $S = 1/2$ spin system with a nondegenerated ground state, $R\ln 2 = 5.76$ J/K mol, and with a doubly degenerated system, $R\ln 4 = 11.52$ J/K mol, respectively. We can find that the extra entropy reaches 7.5 J/K mol at the highest temperature, $T = 300$ K, while about 4.7 J/K mol are released below 100 K, where ΔC has a minimum. The latter entropy released below 100 K is attributed to the metal-insulator and magnetic transition. The value of 4.7 J/K mol is close to $R\ln(2S+1)$ for $S = 1/2$, which means that the degree of freedom for $S = 1/2$ spins is released just above T_{MI}. This supports the hypothesis that the electron occupies the nondegenerate split Hubbard band as suggested in ref. 6.

At higher temperatures, the specific heat of metallic $BaVS_3$ agrees with that of insulating $BaTiS_3$ as seen in

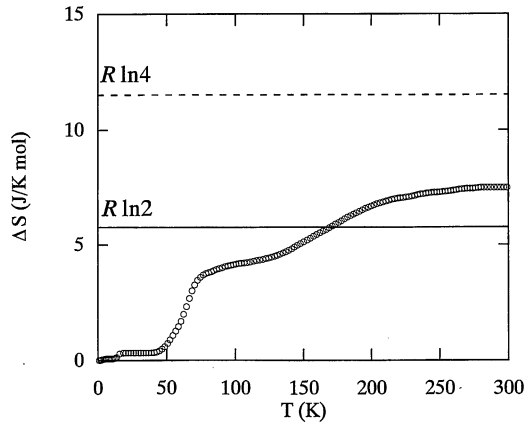

Fig. 4. Extra entropy ΔS of $BaVS_3$ as a function of T.

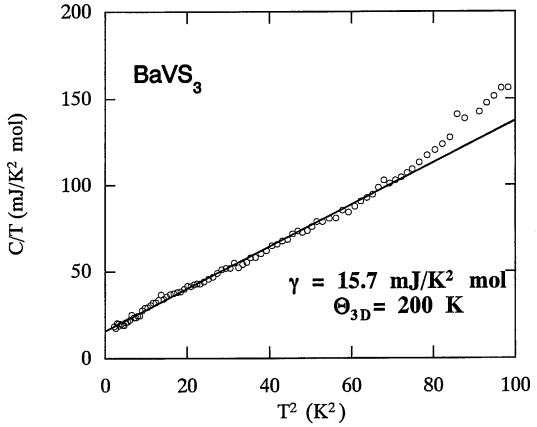

Fig. 5. C/T vs T^2 plot for $BaVS_3$ for 1.4 K< T <10 K (the solid curve is a linear fitting).

Fig. 2. This means that the electronic contribution to specific heat is not represented by the conventional formula γT, in the metallic phase of $BaVS_3$. Taking into account the fact that the paramagnetic moment derived from the Curie-Weiss law is slightly smaller than the 1.73 μ_B expected for $S = 1/2$ of V^{4+}, the paramagnetic state of the metallic phase should be treated in terms of spin fluctuations for nearly localized electrons in narrow bands. In such cases, it is difficult to separate the electronic contribution to specific heat from the magnetic contribution. Therefore, the entropy change at around T_{MI} is considered to be composed of mainly the magnetic entropy for nearly localized electrons, in which the electronic entropy is included.

Above 100 K, the entropy increases again toward the broad peak in ΔC at around 160 K. This may be attributed to thermal excitation to the higher $3d$ levels such as $d_{x^2-y^2}$ or d_{z^2}.[6] These results do not conflict with the Mott transition model proposed for this compound. However, the absence of an entropy change at T_X indicates that the transition at T_X is not a magnetic order-disorder transition.

Figure 5 shows a C/T vs T^2 plot for $BaVS_3$ for $T < 10$ K. A T-linear term of the specific heat is observed in this temperature range. The deduced specific heat coefficient and the Debye temperature are $\gamma = 15.7$ mJ/K^2 mol and $\Theta_D = 200$ K, respectively. The T-linear contribution of the specific heat in the magnetic insulator may occur for various reasons. The most probable origin of $BaVS_3$ is the spin wave excitation for one-dimensional antiferromagnets, which is given as[9]

$$\Delta C = \frac{\kappa N k_B^2}{|J_0|} T, \qquad (1)$$

where κ is a numerical constant (the exact value depends on the theoretical model), N Avogadoro's number, k_B the Boltzmann constant and J_0 the constant of exchange interaction in the one-dimensional chain. Assuming that the anomaly at $T_{MI} = 70$ K corresponds to the specific heat maximum expected for $S = 1/2$ antiferromagnetic Ising chains, we obtained the value of 163 K for $J_0/\ k_B$.[10] Then the specific heat coefficient was determined as $\gamma = 10.1$ mJ/K^2 mol for $\kappa = 0.2$[11] and $\gamma = 17.8$ mJ/K^2 mol for $\kappa = 0.35$,[9] which are comparable to the γ derived from the specific heat measurement. Although there is no direct evidence of occurrence of antiferromagnetic ordering, the present result suggests that the excitation is a gapless one, excluding the possibility of spin-Peierls transition as a mechanism for the metal-insulator transition.

Finally, we discuss complicated behaviors of the low temperature insulator phase, noting the similarity between $BaVS_3$ and the triangular lattice antiferromagnet $CsCoCl_3$, which is isostructural of the high temperature phase of $BaVS_3$, although the low temperature phase of $BaVS_3$ is slightly distorted and hence the triangular lattice of V in the c-plane is not ideal. $CsCoCl_3$ has been extensively studied as a typical frustrated system with antiferromagnetic Ising chains of Co spins.[12] It shows a three-dimensional magnetic order at $T_{N1} = 21$ K. However, a partially disordered antiferromagnetic phase remains below T_{N1} due to propagation of domain wall solitons as a result of frustration. An additional phase transition takes place at $T_{N2} = 9$ K. Below T_{N2} the ferrimagnetic state is realized in which one-third of the chains align in the direction opposite to the direction of alignment of other two-third chains.[13] More interestingly, a specific heat anomaly is detected only at the higher transition temperature T_{N1} and not at T_{N2}.[14] On the other hand, the nuclear relaxation time T_1 exhibits an anomaly at T_{N2}.[15]

In the case of $BaVS_3$, the characteristics of the specific heat and NMR at T_X are analogous to those for $CsCoCl_3$ at T_{N2}, namely, no peak in the specific heat and an anomaly in the relaxation time of nuclear spins. However, the characteristics at T_{MI} of $BaVS_3$ are quite different from those at T_{N1} of $CsCoCl_3$. At T_{N1} $CsCoCl_3$ has no sharp peak in the $\chi - T$ curve due to the one-dimensionality of the magnetic interactions. We can interpret that the sharp peak of $BaVS_3$ occurs as a result of the metal-insulator transition, whose origin is still unknown. Another problem is that the Weiss temperature, Θ, for the metallic phase of $BaVS_3$ is positive (for example, $\Theta = 52.9$ K, 150 K $< T <$ 300 K), which is inconsistent with the antiferromagnetic behavior below T_{MI}. It is plausible that two mechanisms account for the magnetic interactions between V moments one of which

is antiferromagnetic super-exchange via S atoms and the other of which is ferromagnetic interaction mediated by itinerant d electrons. Of course, the latter mechanism disappears in the low temperature insulating phase, giving rise to the predominance of antiferromagnetic interactions below T_{MI}.

In conclusion, we summarize our results of measurements of the specific heat of $BaVS_3$ from 1.4 K to 300 K as follows: 1) A sharp peak in the specific heat was observed at $T_{MI} = 70$ K. The entropy change associated with this peak was estimated to be 4.7 J/K mol, which is close to $R \ln 2$, the expected magnetic entropy for $S = 1/2$. 2) No anomaly was found at T_X, at which some experiments suggest the onset of magnetic ordering occurs. 3) At low temperatures, a T-linear contribution of the specific heat with an apparent γ value of 15.7 mJ/K^2 mol was observed in spite of the absence of conduction electrons. We interpret these results together with those obtained in other experiments as follows: Below T_{MI}, almost all of the entropy associated with the spin freedom of $S = 1/2$ disappears, probably due to the development of one-dimensional antiferromagnetic correlation. The linear term in the low temperature specific heat may be attributed to spin wave excitations for a one-dimensional antiferromagnet. The spin ordering below T_{MI} is not simple and may be successive due to frustration effects characteristic of triangularly arranged linear chains as typically observed in $CsCoCl_3$. It is plausible that the anomaly at T_X is due to the onset of inter-chain magnetic ordering similar to T_{N2} of $CsCoCl_3$.

Although the present interpretations are speculative, we expect a break-through in the elucidaion of the complicated magnetic behaviors of $BaVS_3$ to be achieved through introduction of the concept of frustration into this system.

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