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Structural and magnetic phase transitions of the V_4-cluster compound GeV_4S_8

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The phase transitions of the strongly correlated tetrahedral V_4-cluster compound GeV_4S_8 have been studied by low-temperature powder x-ray diffraction, magnetic susceptibility, and specific heat measurements. The crystal structure is cubic at room temperature (space group $F\bar{4}3m$) and transforms to orthorhombic (space group $Imm2$) at $T_S=30$ K. A Jahn–Teller distortion reduces the symmetry of the V_4-cluster from $\bar{4}3m$ to $mm2$. The second transition at 18 K is the onset of antiferromagnetic ordering without symmetry change but with a certain increase in the distortion. The latter reflects a strong magnetoelastic coupling at T_N. Specific heat anomalies at 30 and 18 K confirm the two phase transitions.

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Strongly correlated chalcogenides with the *fcc* $GaMo_4S_8$ structure represent a new class of Mott insulators in which electronic conduction originates from hopping of localized unpaired ($S=1/2$) electrons among widely separated tetrahedral metal (M_4) clusters.[1] This leads to a variety of unusual transport and magnetic properties. For example, pressure-induced superconductivity occurs in compounds with 4*d* and 5*d* group V elements $GaNb_4S_8$, $GaNb_4Se_8$, and $GaTa_4Se_8$, which reveal the antiferromagnetic correlations at ambient pressure.[2–4] In contrast to this, $GaMo_4S_8$ is ferromagnetic[5] and does not become superconducting even under a pressure of up to 40 GPa.[6] A key aspect of these systems that distinguishes them from conventional Mott insulators (e.g., transition metal oxides) is that the "correlated units" are M_4 clusters rather than single ions. Consequently, these systems exhibit an additional intrinsic lattice degree of freedom that can lead to lattice instabilities and/or structural phase transitions. Indeed, the ferromagnetic insulators $GaMo_4S_8$ ($T_C=26$ K) and GaV_4S_8 ($T_C=13-16$ K) undergo structural phase transitions from cubic ($F\bar{4}3m$) to rhombohedral ($R3m$) symmetry at temperatures $T_S=47$ and 38 K, respectively, well above the onset of magnetic ordering.[7–9] A different situation has been reported recently for the antiferromagnetic cluster compound GeV_4S_8 ($T_N=18$ K) [10] with two unpaired localized electrons ($S=1$). Two successive structural phase transitions have been suggested:[11,12] A structural phase transition from cubic to rhombohedral occurs at $T_S=33$ K, followed by a second transition to an orthorhombic phase at T_N. The observation of this low-temperature structure is in agreement with our previous neutron scattering measurements with GeV_4S_8 at 4.2 K, which showed that the crystal structure of the antiferromagnetic ground state is orthorhombic.[13,14] However, the possible existence of a rhombohedral phase at $T_S=33$ K [11] implies that the onset of antiferromagnetic ordering at T_N is intimately connected with a structural phase transition from a rhombohedral distorted structure into the low-temperature orthorhombic phase, which is in contrast to the above mentioned cluster compounds.

In order to clarify the phase transformations of GeV_4S_8 and its possible relationship to the onset of antiferromagnetic ordering, we have determined the crystal structure at 25 K, which is below the suspected rhombohedral distortion at 33 K, but above the Néel-temperature $T_N=18$ K. In addition, we have performed magnetic susceptibility and specific heat measurements to explore the nature of the phase transitions and their coupling to the lattice. Our results show that the cubic phase at room temperature directly transforms to the orthorhombic structure at $T_S=30$ K and that the onset of antiferromagnetic ordering at $T_N=18$ K occurs without further symmetry reduction but is associated with an increase in the longest V-V bond length. This reflects a strong magnetoelastic coupling at T_N.

Powder samples of GeV_4S_8 were prepared by heating stoichiometric mixtures of the elements as reported previously.[13] Despite the strict exclusion of oxygen during the synthesis, we were not able to suppress traces of V_2O_3 as a by-product in the sample. Powder diffraction experiments were carried out on a Huber G670 Guinier imaging plate diffractometer (Cu-$K_{\alpha1}$ radiation, Ge-111 monochromator, and SiO_2 as external standard), equipped with a closed-cycle He cryostat. Rietveld refinements were performed with the general structure analysis system package.[15] The difficult reflection profiles of the imaging plate detector in combination with the Guinier diffraction geometry were fitted using pseudo-Voigt functions with asymmetry corrections.[16] The V_2O_3 impurity was included in the Rietveld fit. Magnetic measurements were performed using a superconducting quantum interference device magnetometer (MPMS-XL5, Quantum Design Inc.). The data were corrected for sample holder and core diamagnetism by diamagnetic increments[17] and fitted to the Curie–Weiss law. The specific heat was measured from 2 to 100 K by a relaxation-time method in a physical properties measurement system (Quantum Design Inc.).

We first present the structural properties of GeV_4S_8 as obtained from x-ray diffraction measurements. The x-ray diffraction patterns of GeV_4S_8 recorded above 30 K could be

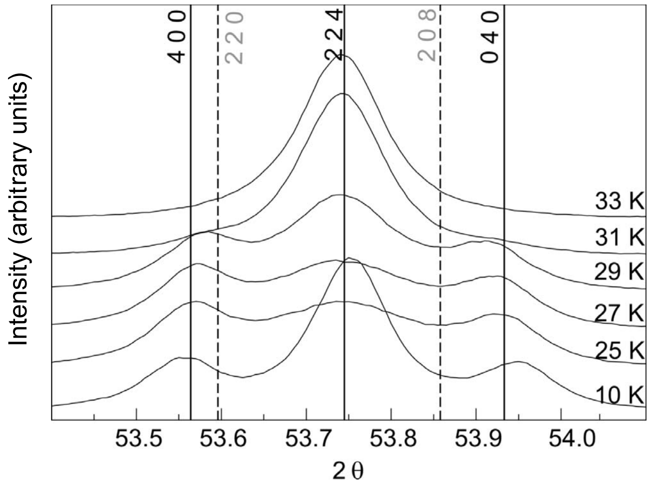

FIG. 1. Cubic (440) reflection and splitting at lower temperatures. Solid lines mark the orthorhombic reflection positions at 25 K, dashed lines mark the assumed rhombohedral reflection positions.

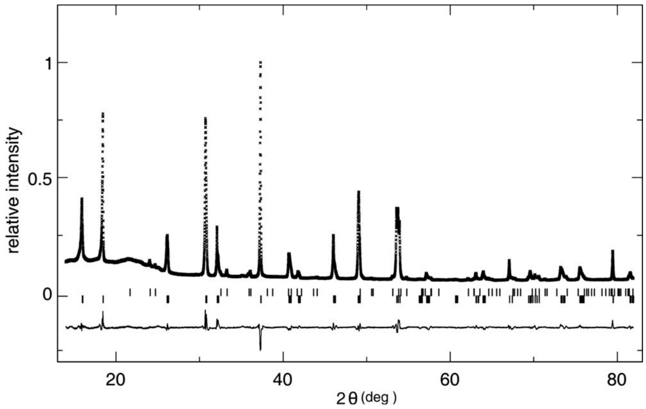

FIG. 2. Rietveld fit of GeV_4S_8 at 25 K. Lower tick marks are GeV_4S_8, upper tick marks the impurity phase V_2O_3

indexed with an *fcc* unit cell according to the space group $F\bar{4}3m$ as described before.[10] On cooling below 30 K, several reflections spilt up or get broader, which clearly indicates a reduction in space group symmetry. A detailed inspection showed that the pattern can be indexed with an orthorhombic unit cell as found for the chemical structure of the magnetically ordered phase below 18 K but not with a rhombohedral cell as proposed by Chudo *et al.*[11] Figure 1 shows the sections of the powder patterns around the originally cubic (440) reflection at low temperatures. The splitting into three reflections between 29 and 31 K is clearly visible. These can be indexed as (400), (040), and (224), whereas a rhombohedral cell would produce only two reflections here, namely, (220) and (208). The increasing divergence of the (400) and (040) reflections, well below the critical temperature, indicates a second-order (continuous) phase transition. This is as expected for a displacive (Jahn–Teller) distortion. Consequently, the space groups above and below the transitions have to be connected by a group-subgroup relation according to Hermann's theorem.[18,19] Therefore, we can rule out a rhombohedral distortion at 30 K by group theory: If the structure is orthorhombic below 18 K and cubic at room temperature, no rhombohedral structure is possible between these two polymorphs because no group-subgroup relation exists between the rhombohedral space group *R*3*m* and the orthorhombic space group *Imm*2.[20]

TABLE I. Rietveld refinement of GeV_4S_8 at 25 K; standard deviation of the last significant digits are given in parenthesis.

Chemical formula	GeV_4S_8
Formula weight	532.84 g/mol
Space group	*Imm*2
Temperature	25 K
a	684.28(1) pm
b	679.94(1) pm
c	964.76(1) pm
V	0.44887(1) nm^3
Z, ρ_{calc}	2, 3.942 g/cm^3
Data points/reflections	13583/166
Variable atomic/profile parameters	13/13
d range	$1.176 < d < 5.581$
R_P, wR_P	0.0307, 0.0441
$R(F2)$, χ^2	0.08252, 4.568
GooF	2.16

Subsequent Rietveld refinements (Fig. 2) using the orthorhombic space group *Imm*2 with starting parameters provided by Müller *et al.*[13] resulted in the structural data summarized in Table I. Refined atomic positions are listed in Table II and selected interatomic distances are given in Table III. The crystal structure of GeV_4S_8 between 30 and 18 K is nearly identical with that of the antiferromagnetically ordered phase below the Néel-temperature.[13] The tetrahedral V_4-cluster units ($\bar{4}3m$ point group) distort by opening one V-V bond from 284.7 (room temperature, cubic) to 287.4 pm and shortening the opposite one to 271.2 pm. The point group of the V_4 unit is reduced to *mm*2. On cooling below the Néel-temperature, we detected a change of the diffraction intensities (see Fig. 1, 10 K plot). This is caused by a further increase in the longest V-V distance inside the cluster up to 290 pm without the change of symmetry and in good agreement with the V-V distances of 290 and 270 pm from neutron diffraction data at 4 K.[13] Thus, the symmetry breaking structural phase transition occurs at 30 K, whereas the onset

TABLE II. Atomic positions of GeV_4S_8 at 25 K.

Atom	Wyckoff position	x	y	z
Ge	2*a*	0	0	0.0037(4)
V1	4*c*	0.2100(4)	0	0.3936(4)
V2	4*d*	0	0.8006(5)	0.5983(3)
S1	4*d*	0	0.7592(7)	0.3691(4)
S2	4*d*	0	0.7293(6)	0.8857(4)
S3	4*c*	0.2577(6)	0	0.6322(5)
S4	4*c*	0.2869(5)	0	0.1283(4)

TABLE III. Interatomic distances in GeV_4S_8 at 25 K.

Ge-S2	216.4(4)	V1-S1	219.1(4)
Ge-S4	230.2(4)	V1-S2	252.5(4)
V1-V1	287.4(5)	V1-S3	232.5(6)
V1-V2	279.4(3)	V1-S4	261.3(6)
V2-V2	271.2(6)	V2-S1	222.9(5)
V1-V1 (intercl.)	396.0(5)	V2-S2	281.5(5)
V2-V2 (intercl.)	408.8(6)	V2-S3	224.8(4)
V1-V2 (intercl.)	402.9(3)	V2-S4	252.7(4)

of magnetic ordering at 18 K is connected with a certain increase in the distortion. Figure 3 shows the three cluster geometries of GeV_4S_8 for comparison.

These structural distortions reflect an interplay between the structure and the magnetism of GeV_4S_8. Figure 4 shows the magnetic susceptibility between 2 and 300 K measured at 1 T. The discontinuity in the $\chi^{-1}(T)$ plot around 170 K is caused by the antiferromagnetic ordering of the V_2O_3 impurity.[21] The Curie–Weiss fit of the data between 40 and 150 K resulted in an effective magnetic moment of $\mu_{\mathrm{eff}} = 2.8 \pm 0.1\mu_B$ (very close to the theoretical value of $2.83\mu_B$ for $S=1$) and a paramagnetic Curie temperature (Weiss-constant) of $\Theta = -40 \pm 2$ K, both in agreement with previous measurements.[10] The susceptibility shows a small drop at ≈30 K followed by a large abrupt decrease at 18 K. The latter is clearly the onset of antiferromagnetic ordering and the origin of the small one, around 30 K, is related to the structural phase transition prior to magnetic ordering. In order to study possible hysteresis effects, we have measured χ with decreasing and increasing temperature at 0.1 T (see insert in Fig. 4). As one might expect, we find a small (≈0.5 K) hysteresis connected with the symmetry breaking structural distortion around 30 K. Surprisingly, a much larger hysteresis (≈2.5 K) is present at the magnetic transition. Such magnetic transitions are typically of second order and, therefore, no pronounced hysteresis is expected. However, in the present case, the onset of magnetic ordering is imminently connected with a structural distortion at T_N, namely, the further increase in the longest V-V bond (see above). This is supported by the neutron diffraction results: The major spin moments in the V_4 cluster are just located at the V atoms obeying the largest V-V distances.[13] Thus, the unusual hysteresis arises from a strong spin-phonon interaction that leads to a strong magnetoelastic coupling at T_N.

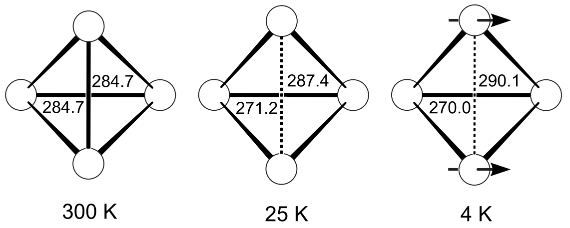

FIG. 3. V_4-cluster units of GeV_4S_8 at 300 ($\bar{4}3m$), 25 ($mm2$, paramagnetic), and 4 K ($mm2$, magnetically ordered). Distances of the longest and shortest V-V bonds are in pm.

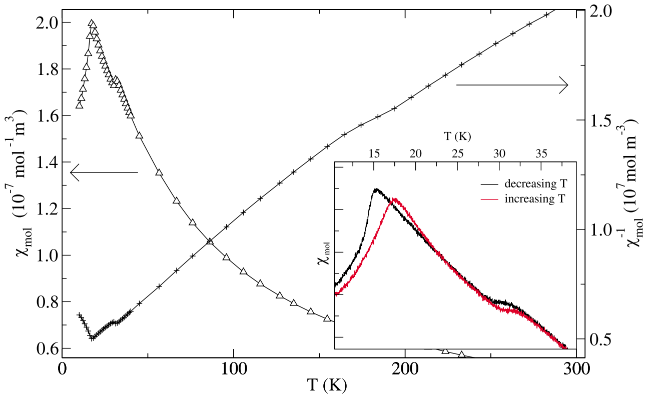

FIG. 4. (Color online) Magnetic susceptibility (△) and inverse magnetic susceptibility (+) of GeV_4S_8 at 1 T. Insert: Hysteresis of the susceptibility measured at 0.1 T. Red (gray) line: increasing temperature; black line: decreasing temperature)

In order to shed a deeper insight into the nature of the phase transitions, we have measured the specific heat C_p with increasing and decreasing temperature. As shown in Fig. 5 (C_p/T as a function of T), both phase transitions cause pronounced anomalies in C_p. We find a small (≈0.5 K) but clearly visible hysteresis for the anomaly connected with the structural transition around 30 K. Moreover, the shape of the anomaly depends on the direction of the temperature sweep. In agreement with the magnetic data, a much larger hysteresis (≈2.5 K) is present at the magnetic transition. The shape of the C_p is typical for a second-order phase transition. However, the pronounced hysteresis points to a first order transition. As shown above, this hysteresis is actually due to a local structural distortion and, thus, a result of the aforementioned magnetoelastic coupling.

A more detailed quantitative analysis of the entropy change at the transition would require a separation of the magnetic and phononic contributions to the total specific heat. A reliable separation is, however, difficult in the case of GeV_4S_8 due to the closeness of the two transitions on one

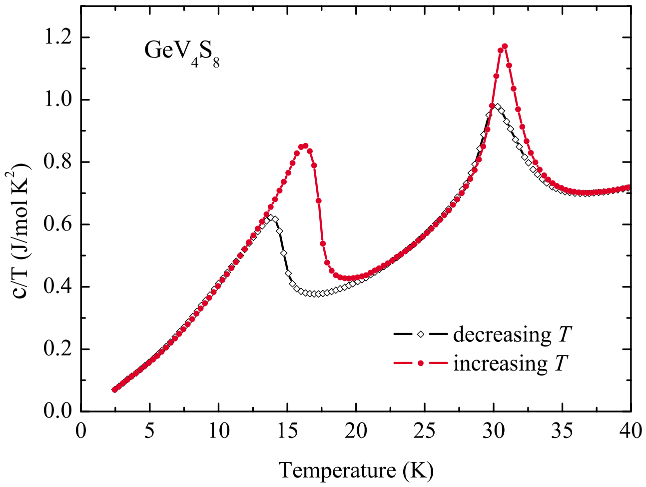

FIG. 5. (Color online) Specific heat of GeV_4S_8. Red (gray) markers: increasing temperature; black markers: decreasing temperature.

hand, and due to the aforementioned magnetoelastic coupling on the other. Therefore, we only consider the total entropy change that can be viewed as a crude estimate of an upper limit of the magnetic entropy change due the magnetic ordering. For the total entropy change up to 20 K, we find about 7.6 J/mole K, which is somewhat smaller than the expected theoretical value $S_{\text{mag}}=N_A k_B \ln(2S+1)=9.1$ J/mole K. Here, $S=1$ is the total spin per V_4 cluster, and N_A and k_B denote Avogadro's number and Boltzmann's constant, respectively. This may be attributed to the correlation effects within the clusters.

In summary, we have shown that the structural transition of GeV_4S_8 occurs at 30 K, well above the antiferromagnetic ordering temperature at 18 K. Thus, both transitions are not simultaneous. The space group symmetry changes from cubic ($F\bar{4}3m$) to orthorhombic ($Imm2$) at 30 K, which corresponds to the structure of the magnetically ordered phase below 18 K. No transformation to a rhombohedral phase is observed as expected from group theory. We find, however, an increase in the longest V-V bond lengths below T_N without a change of the lattice symmetry that reflects a strong magnetoelastic coupling at the magnetic phase transition. Thus, GeV_4S_8 shows a similar behavior as almost all magnetically ordered compounds with $GaMo_4S_8$ structure, where the structural phase transitions always precede to the onset of magnetic ordering. Exceptions are the superconducting compounds $GaNb_4S_8$, $GaNb_4Se_8$, and $GaTa_4Se_8$, where the structural transition and magnetic ordering seems to appear at the same temperature.

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