

Magnetism of Cluster Compounds

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Collaboration with

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Composition and Structure

Structure at room temperature

The formula for this set of compounds is: AM_4X_8

A is a trivalent atom like Ga, Al.

M is a transition metal like V, Mo.

X is a chalcogenide like S, Se.

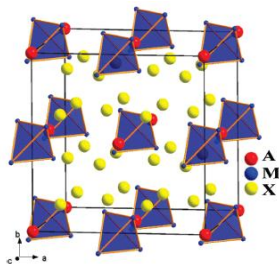


Figure 1. Perspective view of the crystal structure of AM_4X_8 (A = Ga, Ge; M = V, Nb, Ta, Mo; X = S, Se). The M_4 tetrahedral clusters are presented as blue tetrahedra.

The key characteristic of the structure is that M ions form tetrahedral clusters. The M-M distance within cluster is about 30 percent shorter than the distance from the neighboring cluster.

This gives them the name **Cluster Compounds**



Structure

The structure is most conveniently thought of as being composed from two kinds of units: $(M_4X_4)^{5+}$ cubanes and $(AX_4)^{5-}$ tetrahedra. These are arranged in *NaCl* structure. Tetrahedra of metal are in cubane units $(M_4X_4)^{5+}$

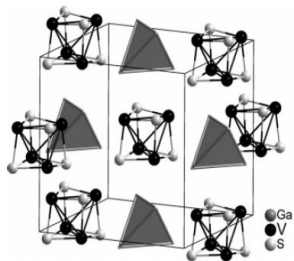


Figure 1. Crystal structure of GaV4S8. The $V_4S_4^{5+}$ cubes and GaS_4^{5-} tetrahedra are emphasized.

Magnetic, thermal and transport properties of these solids have been studied thoroughly. A.K. Rastogi and collaborators have made extensive measurements on $GaMo_4S_8$, $GaMo_4Se_8$, $GaMo_4Se_4Te_4$, GaV_4S_8 , GaV_4Se_8 , AlV_4S_8

Remarkably these exhibit common characteristics, which can be attributed to the clustering of transition metal ions.

They are insulators.

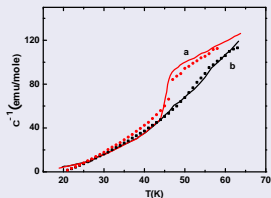
At high temperatures the solids have cubic symmetry and are paramagnetic. They undergo two transitions as the temperature is lowered. First is a first-order structural transition from cubic to rhombohedral phase at temperatures of order 50K.

Second is a transition from paramagnetic to a ferromagnetic phase at temperatures of order 20K.



Magnetic Properties

This slide shows magnetic measurements on $GaMo_4Se_8$



Points to note are:

1. At high temperatures plot χ^{-1} vs temperature show that Curie-Weiss law $\chi = \frac{C}{T+\theta}$ is obeyed.

Curie constant corresponds to a moment of spin half per formula unit i.e. the tetrahedral cluster.

2. Weiss temperature θ is of order 15 K, which means that at high temperatures moments have a weak antiferromagnetic interaction.

3. As the temperature is lowered, the susceptibility shows a rather large jump at a sharp temperature.



3. The X-ray analysis shows that compounds undergo a structural transition at a temperature T_s of the order of 50K. Through a weak distortion the symmetry of the crystal is lowered from cubic to rhombohedral.
4. The susceptibility jump seen above occurs at T_s . Below the structural transition, χ shows a large departure from Curie-Weiss behavior. In particular a marked T^2 -temperature dependence is seen in plots of χ^{-1} .

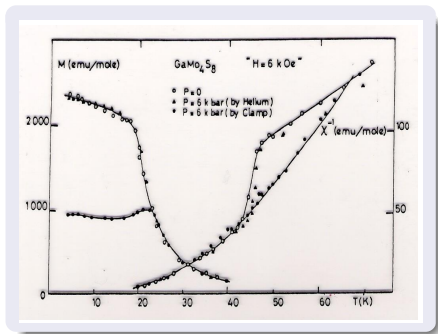


Magnetic Transition

5. Compound undergo another transition at a temperature T_c of the order of 20K, to a ferromagnetic phase.

The saturation moment again corresponds to spin half, which implies that the structural transition affects magnetic interaction strongly, but not the moments.

6. Another interesting feature is the effect of pressure. The hydrostatic pressure has little influence on susceptibility, but the uniaxial pressure wipes out the structural transition.



Magnetic Properties

7. The ferromagnetism does not occur if the structural transition is prevented, say, by introduction of impurities.

8. Another unusual feature of the paramagnetic state below structural transition is rather slow saturation of magnetization with the field. This is seen in relatively smaller slopes of M vs H curves. These are quite unlike a magnet with local moments.

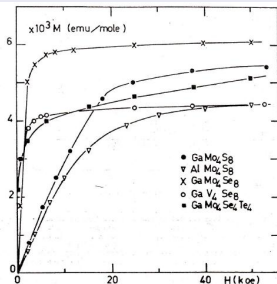


Fig. 3: Magnetisation of 4.2 K for different compounds.

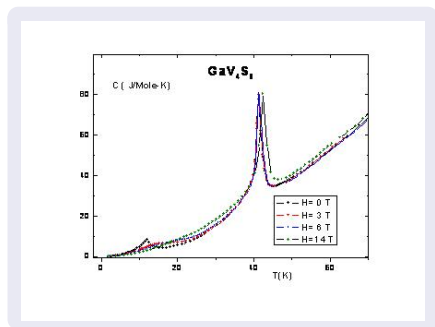
Specific Heat

The specific heat data shown here confirms the existence of two transitions.

There is a large peak at the structural transition characteristic of a 1st order transition.

The second peak occurs at the ferromagnetic transition and is much smaller than the structural peak.

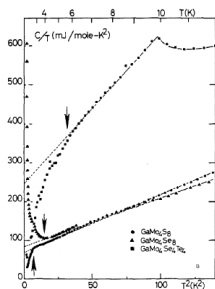
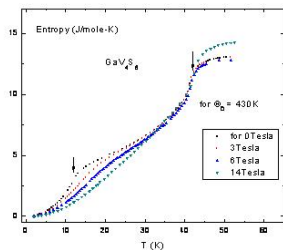
The temperature of the structural transition shifts with magnetic field. Quite remarkably, above T_c specific heat has a large electronic contribution apparently linear in temperature till T_s .



Entropy

In terms of entropy, an entropy of $k_B \log 2$ is recovered at the magnetic transition, consistent with spin-half moments.

An additional entropy of order $k_B \log 4$ is recovered at the structural transition, whose origin is not obvious.



Band Structure Results

The nominal ionic configuration is $A^{3+}(M_4)^{13+}(X_8)^{16-}$, showing that the cluster has odd number of electrons. Thus Mo_4 (V_4) cluster has 11 (7) d-electrons which produce a moment of half.

The band structure studies using Spin-Density Functional Theory with local density approximation (LDA) find the system to be a metal with rather narrow bands near the Fermi level.

States around the Fermi level come largely from d-levels of the transition metal.

Prediction of the metallic nature is wrong, so LDA+U calculations have been performed.

This calculation finds the system to be an insulator, i.e. Mott insulator. A correct moment of $1 \mu_B$ is also obtained for both cubic and rhombohedral structures.

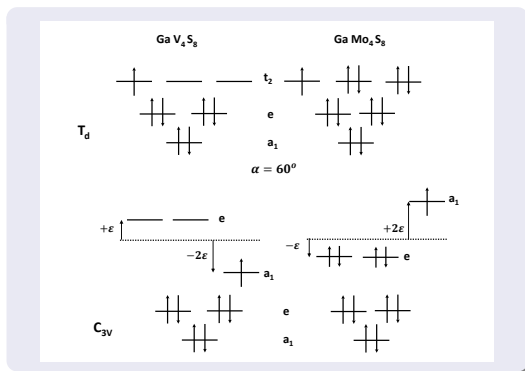


Toward Theory: Electronic Levels of Cluster

To understand the physics of the problem and build a model, it is essential to look at physics at the cluster scale, in particular, the electronic levels of the cluster around the Fermi level.

These come from $(M_4X_4)^{+5}$ cubane unit. In cubic phase there are three levels made up of d-orbitals: a_1 , e and t_2 with degeneracies 1, 2 and 3 as shown here.

V_4 -cluster has 7 d-electrons, so t_2 -level has one electron, while Mo_4 -cluster has 11 d-electrons, so t_2 -level has one hole.



Jahn-Teller Distortion

When electronic levels are degenerate, the interaction between ionic motion and electrons becomes very strong and there is a breakdown of Born-Oppenheimer adiabatic approximation.

In this event the ionic configuration distorts so as to remove the degeneracy of the electronic levels. Distortion lowers the electronic energy, but leads to increase in the elastic energy of the ionic configuration.

The magnitude of the distortion is determined by minimizing these two energies.

R. Pocha, D. Johrhardt and R. Pöttgen, Chem. Mater. 12, 2882 (2000)



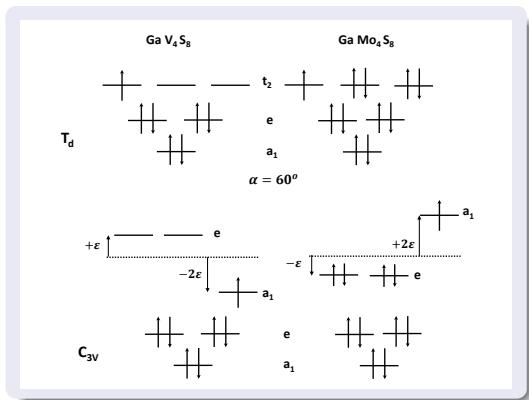
Jahn-Teller Distortion

In our situation, distortion causes a splitting of t_2 -level into e_g and a_1 levels.

This leads to distortions of different signs for V_4 and Mo_4 compounds

For V_4 one axis is stretched to lower a_1 -level occupied by the electron, whereas for Mo_4 one axis is compressed so as to raise a_1 -level occupied by the hole.

This is exactly what is observed.



Structural Transition

For us the key point to note is that an isolated tetrahedron can suffer the above distortion in 4 ways, corresponding to any one of the four vertices moving in or out.

Energy gained in JT distortion is of the order of 0.1 to 0.2 eV, much larger than the thermal energy at temperatures of interest.

Due to relative isolation of tetrahedra in this structure, the distortion energy is larger than the interaction energy between tetrahedra.

So we surmise that the distortions of tetrahedra occurs at some temperature higher than room temperature and the system is in a para state of distortions with each tetrahedron flipping between four equivalent distortion states with zero net distortion.

Distortion axes get aligned cooperatively at T_s due to elastic as well as orbital interactions. This mechanism gives an additional high temperature entropy to be $k_B \log 4$ per cluster.



Structural Transition

This is a novel mechanism for the structural transition in these solids. We model this transition by a 4-state Potts model.

The four axes of distortion in a tetrahedron are described by vectors \vec{v}_τ which are unit vectors that join the center of a tetrahedron to its vertices, with $\tau = 1$ to 4, corresponding to the vertex that has been pushed in (out).

Unit vectors \vec{v}_τ are: $(1, 1, 1)/\sqrt{3}$, $(1, -1, -1)/\sqrt{3}$, $(-1, 1, -1)/\sqrt{3}$, $(-1, -1, 1)/\sqrt{3}$, with the property $\vec{v}_{\tau_1} \cdot \vec{v}_{\tau_2} = (4\delta_{\tau_1, \tau_2} - 1)/3$.

Due to interactions, the strains produced by distortions interact. The strain energy favours alignment of distortions, so we may write this energy as,

$$H_S = - \sum_{(i,j)} K(i,j) \vec{v}_{\tau_i} \cdot \vec{v}_{\tau_j}$$



Model

For $K(i, j) > 0$ same distortion on neighbouring tetrahedra have lower energy compared to dissimilar distortions. So this Hamiltonian favours a ferro distorted state at lower temperatures. It gives rise to a first-order transition from para to ferro state.

Now we consider magnetic interaction between spins.

The magnetic interaction between neighbouring cells arise due to kinetic exchange. This interaction is strongly affected by distortions, as it is very sensitive to the degeneracy of the levels and overlap integrals. One adds to the Hamiltonian the magnetic exchange term.

$$H = - \sum_{(i,j)} J_{ij}(\tau_i, \tau_j) \vec{S}_i \cdot \vec{S}_j$$

The exchange interactions depends on the distortion axes of the tetrahedra.

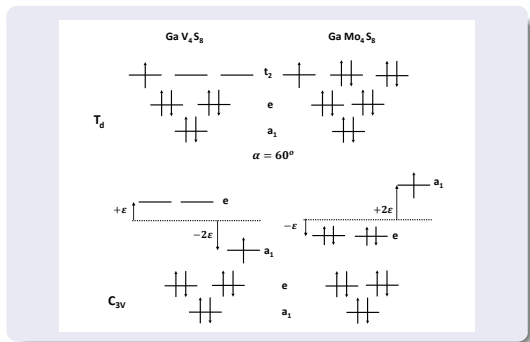
For nondegenerate levels the kinetic exchange is antiferromagnetic and is given by $-4t^2/U$.



Magnetic Interactions

With degeneracy there are several intermediate states and a more complicated interaction.

Using the notation: t_{aa} and t_{ae} hopping amplitudes between a to a and a to e. Δ denotes the energy difference between a_1 and e_g levels. U_{aa} Coulomb interaction for two electrons on a-level, U_{ae} and J_{ae} are direct and exchange Coulomb interaction between a and e levels.



$$J = 4 \left[\frac{2J_{ae}t_{ae}^2}{(U_{ae} + \Delta)^2 - J_{ae}^2} - \frac{t_{aa}^2}{U_{aa}} \right]$$



The key quantities which are affected by distortions are the hopping amplitudes t 's as they depend on the overlap of wavefunctions between clusters. So we assume

$$\begin{aligned}t_{aa}(R_{ij}, \tau_i, \tau_j) &= t_{1a}(R_{ij})\delta_{\tau_i, \tau_j} + t_{2a}(R_{ij})(1 - \delta_{\tau_i, \tau_j}) \\t_{ae}(R_{ij}, \tau_i, \tau_j) &= t_{1e}(R_{ij})\delta_{\tau_i, \tau_j} + t_{2e}(R_{ij})(1 - \delta_{\tau_i, \tau_j})\end{aligned}$$

Using these one finally arrives at a Hamiltonian of the form

$$H = - \sum_{(i,j)} [K(i,j)\vec{v}_{\tau_i} \cdot \vec{v}_{\tau_j} + J_H(i,j)\vec{S}_i \cdot \vec{S}_j + J_c(i,j)(\vec{S}_i \cdot \vec{S}_j)\vec{v}_{\tau_i} \cdot \vec{v}_{\tau_j}]$$

Here $J_H < 0$, so basic spin-spin interaction is antiferromagnetic. $J_c > 0$ and this ultimately leads to the ferromagnetic transition depending on the distortion state. Interactions are taken only between nearest neighbours.



Mean Field Approximation

We have analysed this model using mean-field approximation. We introduce two order parameters: $\langle \vec{v}_{\tau_i} \rangle = \psi \vec{v}_1$ and $\langle \vec{S}_i \rangle = \frac{m}{2} \vec{z}$. This leads to the free energy

$$\begin{aligned} F/N &= -z(K\psi^2 + J_c\psi^2 m^2 + J_H m^2)/2 \\ &+ K_B T \left[\frac{1+3\psi}{4} \log \left(\frac{1+3\psi}{4} \right) + \frac{3(1-\psi)}{4} \log \left(\frac{1-\psi}{4} \right) \right] \\ &+ K_B T \left[\frac{1+m}{2} \log \left(\frac{1+m}{2} \right) + \frac{1-m}{2} \log \left(\frac{1-m}{2} \right) \right] \end{aligned}$$

z denotes the number of nearest neighbours. For our choice of parameters, this model gives rise to two transitions. One first-order corresponding to structural transition at T_s and second, a continuous transition to ferromagnetic state at T_c .



Mean-field approximation is not adequate to understand the experimental data, especially for properties like specific heat, for which one needs to account for short-ranged correlations. However, it gives a qualitative account of the behaviour which acts as a useful guide to understand the better theory.

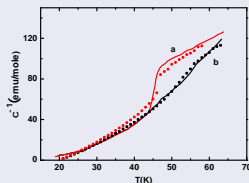
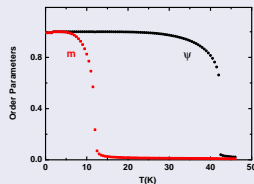
So we have performed Monte-Carlo simulation, on a lattice of $20 \times 20 \times 20$ sites. The main simplification made is to use Ising instead of Heisenberg interaction, which gives us 8 states for each site.



Monte-Carlo Simulation Results

Dependence of order parameters with temperature. Structural order parameter ψ , Magnetization m

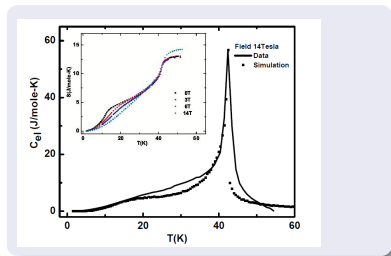
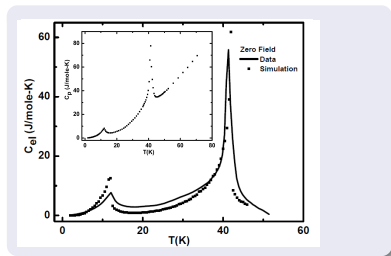
Behaviour of Inverse Susceptibility with temperature. The jump in susceptibility arises as the effective interaction changes from $J_H < 0$ to $J_H + J_c\psi^2 > 0$ and ψ is discontinuous at T_s . The departure from Curie-Weiss behavior arises partly due to temperature variation of ψ .



Monte-Carlo Simulation Results

Electronic Specific Heat with Temperature. line: experiment; dots: MC simulation.

Specific Heat in Magnetic field and Entropy. High temperature entropy $R \log 8$.



Summary

Cluster compounds present a set of rather puzzling magnetic and thermodynamic properties.

Basic features of these properties are common to a number of compositions and are attributable to the presence of tetrahedral clusters of transition metal ions.

Key to understanding their behavior lies in examining the local electronic levels in a cluster.

This leads us to bring under consideration the orbital degrees of freedom.

Due to clustering local distortions can occur in a degenerate way, which is not usually possible in other structures, like perovskites.



A quantitative explanation is obtained for the following observed features.

1. Mechanism of Structural transition and the origin of the high-temperature entropy.
2. Discontinuous jump in the magnetic susceptibility at the structural transition and its departure from Curie-Weiss behavior above T_c .
3. Change of magnetic interaction from weakly antiferromagnetic to ferromagnetic.
4. Difference in the specific heat peaks at the two transitions and the origin of its large non-phononic contribution.
5. Behavior of susceptibility under uniaxial pressure and shift of structural transition by magnetic field.



Thank you

Ref: Euro. Phys. Lett. 101,67008 (2013)

