Chapter - V

Transport properties of V₄-cluster compound
Ga₁₋ₓCuₓV₄S₈

Introduction

The electronic properties of GaV₄S₈ are dominated by strong correlations and are intimately related to its peculiar crystal structure. GaV₄S₈ belongs to a family of cluster compounds, which are introduced in chapter-I. It showed hopping conduction, an electronic transition and change in structure at 45K temperature and became ferromagnetic below 13K [1, 2, 3]. These compounds are derived from deficient spinel of the form A₀.₅B₀.₅X₄ in which the ordering of Ga-vacancies (□) on the tetrahedral ‘A’ sites reduces the space group of spinel from that of diamond lattice Fd3m to F43m [4, 5].

There is an alternate way for the description of crystal structure for the vacancy ordered A₀.₅B₀.₅X₄ phases. We can write the chemical composition Ga₀.₅V₂S₄ as GaV₄S₈ and then describe the structure as built up by molecular units [GaS₄]⁻⁵+[V₄S₄]⁺⁵ arranged on a NaCl – type lattice. The most important aspect of the structure is that the V- atoms (occupying the B – sites of spinel) shift from their usual octahedral position to form tetrahedral V₄ cluster within the cubic units V₄S₄. These modification of the structure results in intra cluster V distances as in vanadium metal (less than 3 Å), but the inter-cluster V₄-V₄ distances are now more than 4 Å. These large inter-cluster distances render this compound a Mott–insulator. Because of clustering, the molecular orbitals on V₄S₄ units are highly degenerate. The effect of highly degenerate orbitals on the correlations among the electrons on different clusters are remarkably different than for the electrons in a narrow band solid, such as V₂O₃ and high temperature superconductors etc. which are at the boundary of Mott–insulators.

Within the ionic configuration Ga⁺³V⁺³.₂⁵S⁻² each V₄ cluster contains seven valence electrons. The unpaired electron per cluster is responsible for the para-magnetism and the
ferromagnetism below 13K. N. Santhi et al. have calculated the band structure of isostructural GaMo$_4$S$_8$ containing Mo$_{12}$-clusters [6].

Here I focused on the electrical conductivity and thermopower of high quality polycrystalline materials of pure and Cu-substituted V$_4$-cluster compounds. Our sintered pellets of GaV$_4$S$_8$ are single phase with superior crystalline order and showed much sharper anomaly at the structural phase transformation temperature at 45K as reported previously by Y. Sahoo and A. K. Rastogi [7, 8].

### 5.1 Sample preparation and structural analysis

These compounds had been previously prepared by Y. Sahoo in our labs using direct reaction of the pure elements and by Majid A. Ruman using H$_2$S reduction of corresponding oxides. For my study I have prepared the compounds of GaV$_4$S$_8$ and Ga$_{0.90}$Cu$_{0.10}$V$_4$S$_8$ using same method as Y. Sahoo. But we got much better ordered crystalline powders by using lower temperature and for much longer time for the sintering of final products than used by Y. Sahoo. The better crystalline order is inferred from relatively sharper peaks in our x-ray diffraction pattern as well as sharp anomalies observed in conductivity, thermopower (reported in the following sections) and in magnetic susceptibility at 45K transition.

For the preparation, stoichiometric mixture of Ga = 99.99%, Cu = 99.999%, V = 99.7% and S = 99.999% are slowly heated in the sealed quartz tube in 10-15 days up to 750°C. Reacted powder is then pulverized in a mortar and pestle inside a dry box. The circular pellets are made at pressure of 8 Ton in a hydraulic press. The final sintering of the pellets is done at 800°C for seven days in an evacuated sealed quartz tube. The Ga$_{0.80}$Cu$_{0.20}$V$_4$S$_8$ is prepared by re-mixing the two sintered pellets of Ga$_{0.50}$V$_2$S$_4$ and CuV$_2$S$_4$ at the ratio of 9:1. The sintering of its pellets (made at 8 ton pressure) is also done at same temperature of 800°C for one week. It is worth while to remark that similar compounds made by Majid at higher temperature of 950°C resulted in hexagonal polymorphs with completely different electronic properties [9].
Fig. 5.1: X-ray diffraction pattern of $\text{Ga}(1-x)\text{Cu}_x\text{V}_4\text{S}_8$ ($x = 0, 0.10 \& 0.20$) at room temperature. The tiny peaks marked '?' for 20% Cu are due to impurity phase.

**X-ray diffraction:** The X-ray diffraction was done at room temperature to identify the structure and phase of the samples. The peaks found from the X-ray diffraction measurement are indexed in fig. 5.1. Either all even or all odd miller indices of the cubic unit cell indicated the FCC structure [10]. The presence of extra peaks 200, 420 and 640, which are forbidden for the spinels (also for diamond lattice) is due to the 1:1 ordering of the vacancy and occupied sites by Ga (or Cu) in the tetrahedral A-sites of the spinel. The cubic lattice constant was $a = 9.662\text{Å}$ for the pure cluster compound of $\text{GaV}_4\text{S}_8$. 

90
which showed slight change in $a = 9.660\,\text{Å}$ for the 10% Cu-substituted compound as given in the table – 5.1. The lattice parameter is same as found by Sahoo and Majid for the same compound prepared differently. In contrast to the quite broad peaks for the $\text{H}_2\text{S}$-reduced phases prepared by Majid and also found to be non-stoichiometric- sulfur deficient, the x-ray diffraction pattern of my compound gave excellent single phase of high crystalline order, when prepared at relatively low temperatures by the direct reaction of elements. The X-ray diffraction results of all the compounds are given in the Appendix-A.

5.2 Electronic Properties

The electrical resistivity was measured on all the polycrystalline materials from 2 to 600K by using van der Pauw method [11]. We are unable to measure the resistivity down to 36K in GaV$_4$S$_8$ where it becomes more than 10MΩ. Seebeck-coefficient measurement was carried out by the dc differential method using a lab-made thermo-electric power setup in a close cycle He- refrigerator from 16 to 300K. In this compound we are unable to measure ‘S(T)’ below 30K due to noisy thermoelectric voltage because of high resistivity.

5.3 Transport properties of GaV$_4$S$_8$

5.3.1 Resistivity

The resistivity data for two samples of GaV$_4$S$_8$ (sample-1 annealed at 800°C and sample-2 annealed at 500°C) are plotted as log ($\rho$) versus $1/T$ from 30K to 600K temperature range in fig. 5.2. I here report resistivity of GaV$_4$S$_8$ for the first time from room temperature to 600K.

On cooling from 600K, the resistivity follows an Arrhenius dependence ($\log(\rho) \sim 1/T$) with the same slope for both the samples. The room temperature resistivity of both the samples is about 4 $\Omega$-cm. From the slope of $\log\rho$ versus $1/T$ between 300K to 600K, we estimate activation energy $\sim 0.157$ eV. This is same as previous results [7]. There is a
clear changeover in the temperature dependence around 250K. Below this temperature the plot is non-Arrhenius and shows a downward curvature, meaning a continuous reduction in the activation energy. In the following we will discuss the origin of this behavior. At 45K for sample-1 and 43K for sample -2, a phase transformation anomaly is observed. The resistivity at this temperature showed a sharp downward jump on cooling, followed by a nearly linear log(\(\rho\)) versus 1/T dependence in the low temperature phase. This electronic phase transition is accompanied by structural transformation—Cubic to Rhombohedral—without any volume change [4]. I see that the sample –2, which was re-annealed at a lower temperature and is, expected to have better crystalline order, showed a sharper transition albeit at a lower temperature.

Fig. 5.2: Arrhenius plot (log(Resistivity) vs. 1/T) of the GaV\(_4\)S\(_8\). In the inset the effect of strong magnetic field on the anomaly around 43K transition is shown.
Although grossly, the temperature dependence reported previously on GaV₄S₈ by Y. Sahoo is similar, the sharpness of the resistivity anomaly at 45K transition in my compounds and a downward jump was absent from his results. This is no doubt due to the sensitivity of conduction properties on disorder and the crystalline imperfections in these compounds, which seems to increase for the samples prepared at higher temperature by Y. Sahoo. This can also be seen in fig. 5.2, where differently annealed samples show significant difference in the conduction behavior in the temperature range of 36K to 250K, including the transition around 45K. The perceptible difference in the conductivity behavior of samples prepared by H₂S reduction of oxides and by elements has already been reported in detail by Majid [9]. He found that for the non-stoichiometric phases obtained by H₂S reduction of oxides the dependence (log(\(\rho\)) \(-\frac{1}{T} 1/4\)) extends over to a much higher temperature compared than 250K for the stoichiometric compositions obtained by direct synthesis from the elements. This is due to broadening of the band of localized electrons because of increased disorder in non-stoichiometric phases. In the inset fig. 5.2, I have shown the effect of magnetic field on this transformation anomaly around 45K for sample -2.

5.3.2 Seebeck Coefficient

In fig. 5.3 I have plotted the Seebeck coefficient ‘S’ as a function of temperature of sample-1 in the temperature range of 36K to 300K. The Seebeck coefficient is negative and equals \(-320\mu V/K\) at 300K. It increases in magnitude with decreasing temperature passing to about \(-750\mu V/K\) around 100K, where it shows a broad maximum. Our temperature dependence behavior of Seebeck coefficient of GaV₄S₈ is quite similar to the previously reported results of Y. Sahoo and A. K. Rastogi [7, 8], although the magnitude of thermopower is much larger in our case.

I also present, for the first time, the behavior of the Seebeck coefficient around the transition at 45K. For this measurement special additional filter circuit was designed and used as already explained in chapter-II. ‘S’ decreases on cooling below 100K, with the jump like drop at the transition temperature from \(-440\mu V/K\) to a large positive value. The
jump-like changes are also seen in other electronic properties — electrical resistivity (see fig. 5.2) and magnetic susceptibility at this transition [1, 2]. On cooling through the transition resistivity shows a downward jump while the magnetic susceptibility value is approximately doubled. In the low temperature phase the rhomohedral distortion is very slight as $a_R = 6.8\AA \approx \frac{a_c}{\sqrt{2}}$ and $\alpha \approx 59.6^\circ$ is near to $60^\circ$. However there is dramatic increase in ferromagnetic interactions. The true nature and the physical mechanism of this electronic transition are still not understood.

I can compare thermopower with the conductivity property, which was found to be activated with $\ln (\rho) \sim (1/T)$ dependence above 250K. I plotted the Seebeck coefficient as $S/(k_B/e)$ versus $1/T$ along with the resistivity in fig. 5.4. In case of an extrinsic semiconductors $S(T)$ is given by the relation (5.3a). And the slope of this plot would give activation energy $E^s_{act}$ for the generation of carriers. This slope is same as for the slope of resistivity when carriers are in a wide band.

$$S = \frac{k_B}{e} \left[ \frac{E^s}{k_B T} + \text{cons tan } t \right]$$

(5.3a)

The $S(1/T)$ does not follow this dependence below room temperature. We recall that $E^{0}_{act} = 0.17$ eV in the resistivity between 250K and 600K. The above relation completely fails to explain the $S(T)$ dependence below 250K. A detailed study of the transport properties of pure and Zn substituted compounds has been made by Y. Sahoo [8]. He has shown that in these cluster compounds non- Arrhenius $\rho(T)$ and $S(T)$ behavior is due to hopping conduction of the carriers localized on the V$^+$ clusters. In this case there is no energy gap at the Fermi level and so the activation energy for the generation of the current carriers is zero. However an activation energy in the conductivity is required for the mobility of the localized carriers because of phonon assistance for the hopping event. The thermopower, however, is not directly related to the mobility of the carriers and so the activation is not measured in the thermopower.

This interpretation in terms of hopping conduction is also consistent with the strong frequency dependence of ac – conductivity found in this and other cluster compounds [7, 8, 12].
Fig. 5.3: Seebeck coefficient of GaV$_4$S$_8$ specimen. Thermopower is negative and increases on cooling. A sharp jump to positive values is seen at 45K transition.

Fig. 5.4: Resistivity and thermopower dependence on temperature plotted to show the activated transport in GaV$_4$S$_8$. 

95
5.4 Transport properties of Ga$_{1-x}$Cu$_x$V$_4$S$_8$

5.4.1 Resistivity

The resistivity data for Cu-substituted V$_4$-cluster compounds of Ga$_{0.90}$Cu$_{0.10}$V$_4$S$_8$ and Ga$_{0.80}$Cu$_{0.20}$V$_4$S$_8$ in the temperature range of 2 to 600K are plotted in fig. 5.5 on a semi-log scale. Substitution of Cu for Ga results in reduction of resistivity. The resistivity increases on cooling, but in contrast to the nearly Arrhenius behavior, Ln(\(\rho\)) \sim 1/T, above 250K for the pure phase (see fig. 5.2) which gave an activation energy of 0.17 eV, here behavior remains non-Arrhenius throughout the entire range of measurements. We can, however, estimate an activation energy of about 0.08 e.V. around room temperature and above.

Fig. 5.5: The resistivity behavior of Cu - substituted V$_4$ - compounds, plotted on Log(\(\rho\)) versus temperature in order to clearly show the anomalous behavior around 150-170K.
Anomaly at 160K: There is a clear changeover in the temperature dependence below around 150-170K. It may be possible that this anomalous conductivity behavior is related to a phase change when around 20% Cu substitutes Ga as seen with a clear jump on cooling and a hyseresis in 20% Cu sample. We remark that the similar behavior with much larger jump in the resistivity was found by Majid in case of more than 15% Cu – substituted samples prepared (using H₂S – reduction method) [9]. This result should be carefully verified on more specimens, since we do not find corresponding changes in thermopower as well as magnetic susceptibility of this composition. This change over in the conductivity as well may be of similar nature as found around 250K in our pure phase. In the pure phase Sahoo and Rastogi has attributed this change as a cross over from near neighbor hopping to the variable range hopping conduction at low temperature. In fig. 5.6, we show the conductivity plots using Motts variable range expression \( \ln(\rho) - (1/T)^{1/4} \).

Fig. 5.6: Hopping conductivity of V₄ - cluster compounds. Showings cross over from near neighbor hopping to variable range hopping below 150K - 250K.
5.4.2 Seebeck Coefficient

In fig. 5.7, we show the Seebeck coefficient dependence on temperature for pure and Cu-substituted V₄-cluster polycrystalline samples from 16 to 300K. By substituting 10% of Cu on the Ga-site in the pure sample, the sign of the ‘S’ is changed from negative to positive at room temperature. In our Cu-substituted V₄-cluster compounds, ‘S(T)’ decreases below 240K on cooling after a broad maximum around 280K. As the Cu-concentration increases the maximum around 280K becomes sharper as we found in our 20% Cu-substituted sample compare to the 10% Cu-substituted sample. Below 125K the ‘S(T)’ of these samples are very close to the zero. The nature of variations with respect to temperature of the above specimens (Ga₀.₉₀Cu₀.₁₀V₂S₄ and Ga₀.₈₀Cu₀.₂₀V₂S₄) is very similar with the reported results of the Ga₀.₈₅Cu₀.₁₅V₄S₈ compound with rhombohedral symmetry [9].

![Graph showing Seebeck coefficient vs. temperature for different compositions](image)

Fig. 5.7: Absolute S(T) vs. temperature of the Ga₁₋ₓCuxV₄S₈ (x = 0.0, 0.10 & 0.20). Left y-axis is used for GaV₄S₈ but right y-axis is used for Ga₀.₉₀Cu₀.₁₀V₂S₄ and Ga₀.₈₀Cu₀.₂₀V₂S₄.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\text{GaV}_4S_8$</th>
<th>$\text{Ga}<em>{0.90}\text{Cu}</em>{0.10}\text{V}_4S_8$</th>
<th>$\text{Ga}<em>{0.80}\text{Cu}</em>{0.20}\text{V}_4S_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>9.662</td>
<td>9.660</td>
<td>9.660</td>
</tr>
<tr>
<td>$\rho_{300}$ ($\Omega \cdot \text{cm}$)</td>
<td>4.275</td>
<td>0.479</td>
<td>0.224</td>
</tr>
<tr>
<td>$S_{300}$ ($\mu \text{V} / \text{K}$)</td>
<td>-323.58</td>
<td>+53.79</td>
<td>+58.95</td>
</tr>
<tr>
<td>$E_{\text{act.}}^{0\text{pl}}$ (eV)</td>
<td>0.157</td>
<td>0.080</td>
<td>0.080</td>
</tr>
<tr>
<td>$T_g(K)$</td>
<td>$63.76 \times 10^6$</td>
<td>$0.77 \times 10^3$</td>
<td>$1.23 \times 10^3$</td>
</tr>
<tr>
<td>$T_d(K)$</td>
<td>45</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$T_d'(K)$</td>
<td>258</td>
<td>157</td>
<td>169</td>
</tr>
</tbody>
</table>

$T_d(K) = \text{Cubic to Rhombohedral transition temperature}$

$T_d'(K) = \text{Resistivity changeover temperature}$

### 5.5 Discussion

From our experimental results, we found the lattice constant $a = 9.662$ Å for pure $\text{V}_4$-cluster compound same as reported previously, which is not affected very much by the substitution of 10% Ga by Cu. For pure phase, $\log(\rho) \sim 1/T$ above 250K, which gives an activation energy of 0.16eV. The transport properties of these compounds are qualitatively different from the wide band semiconductors. We compared the transition at 45K found in our measurement related to the cubic to rhombohedral phase transition with the previous results and conclude that it is very sensitive to the purity of the $\text{GaV}_4S_8$ specimen of powder polycrystalline sample. From fig. 5.2, we showed the two anomalies at 258K and 45K with gradual decrease of activation energy going down to the lowest temperature for $\text{GaV}_4S_8$ specimen. This type of variation in activation energy was found in the disordered materials due to the hopping conduction mechanism, where the conduction is by nearest neighbor hopping at higher temperature but as the temperature decreases the conduction is by hopping between the longer distances as a result the activation energy $E_{\text{act.}}^{0\text{pl}}$ decreases with the temperature [13, 14]. The Ferromagnetic transition was not found in the resistivity measurement of Cu-substituted cluster compounds within our measurement range at low temperature.
The perceptible difference in the conductivity behavior of samples prepared by H$_2$S reduction of oxides and by elements has already been reported in detail by Majid [9]. It was found that non-stoichiometric phases were obtained by H$_2$S reduction and the dependence ($\log(\rho) \sim 1/T^{1/4}$) extends over much higher temperature.

5.5.1 Magnetoresistance

The inset fig. 5.8 was plotted in Resistance vs. temperature of GaV$_4$S$_8$ specimen at 0Tesla and 6Tesla field around the phase transformation temperature. The resistance was found independent of the external magnetic field except in the region of phase transformation temperature. Fig. 5.8 shows the $\text{MR} = [R(6, T) - R(0, T)] / R(0, T)$ vs. temperature of GaV$_4$S$_8$ around the phase transformation anomaly. Starting from the high temperature side of 43K, the magnitude of the MR slowly increases with decreasing temperature. Below 42K it rises very rapidly to attain a broad maximum around 41K and then decreases sharply.

![Magnetoresistance vs. temperature of the GaV$_4$S$_8$ around phase transformation temperature. In the inset the effect of strong magnetic field on the anomaly around 43K transition is shown.](image)

Fig. 5.8: Magnetoresistance vs. temperature of the GaV$_4$S$_8$ around phase transformation temperature. In the inset the effect of strong magnetic field on the anomaly around 43K transition is shown.
5.6 Conclusion

Previous studies by M. M. Abd-Elmeguid et al showed the transformation of Mott-insulator to metallic behavior and superconductivity in GaNb$_4$S$_8$ and GaNb$_4$Se$_8$ by applying the external pressure [15]. They concluded that the distorted octahedral site of ‘Nb’ is transformed to undistorted position by external pressure. But in our case we study the Mott variable range hopping (VRH) conduction and phase transformation by substituting Cu ions in the pure specimen without disturbing the octahedral atoms. The octahedral atoms play the vital role for the variable range hopping conduction mechanism, due to the localized conduction electrons at the Fermi energy. We found the variable range hopping conduction in our Cu-substituted compounds with the absence of phase transformation temperature within our measurement regions. The 258K anomaly of the pure compound is shifted to 157K for Ga$_{0.90}$Cu$_{0.10}$V$_4$S$_8$ compound. To know the mechanism of this anomaly, we have to study further.
References