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Evidence of hopping conduction in the V₄-cluster compound GaV₄S₈

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Abstract. The electrical resistivity and Seebeck coefficient of ferromagnetic semiconductors GaV₄S₈ and GaV₄Se₈ between 20 K and 350 K have been measured. These compounds have a cation-deficient spinel composition with Gallium-vacancy ordering and clustering of vanadium atoms into metallic bonded tetrahedra. For the stoichiometric phase, the Arrhenius plots of resistivity show a strong downward curvature; the activation energy E_a^0 of GaV₄S₈ varies from 0.14 eV at room temperature to 0.04 eV at 80 K. We also report AC conductivity measurements between 400 Hz and 200 kHz on stoichiometric GaV₄S₈. We find that the $\sigma_{AC}(\omega, T)$ behaviour is similar to that of a Fermi glass and $\sigma_{AC}(\omega) \sim \omega^s$; $s = 0.3$ – 0.8 between 50 and 20 K. The substitution of sulphur by selenium or imperfect ordering of Ga vacancies results in a constant E_a of about 0.13 eV over a wide temperature interval. The thermopower behaviour is very sensitive to the quality of the sample and indicates charge transport in a narrow band. These properties are discussed in relation to the special structural features of cluster compounds.

1. Introduction

The compounds of the present study have a cation-deficient spinel composition $A_\delta B_2 X_4$ with $\delta = 0.5$. For trivalent Al or Ga, a 1:1 order among the occupied and vacant tetrahedral sites of spinel structure is observed. Consequently the space group symmetry $Fd3m$ of spinel structure is lowered to $F\bar{4}3m$. In addition, the detailed x-ray analysis reveals the formation of B-atom metal clusters for Mo, V, Nb and Ta but not for the Cr compounds. In cluster compounds, there are two B–B distances. The intracenter distance is nearer to the metallic bonding distance and gives a tetrahedral arrangement of B atoms. The intercluster distance is much larger ($> 4 \text{ \AA}$) and depends on the size of the anions. The electronic band-structure calculations of these compounds have not been carried out so far, but the semiconducting behaviour observed in all of these compounds has been attributed to the large intercluster separation of B atoms [1–4].

The clustering of transition-metal atoms results in distinct magnetic properties, as opposed to that observed in common spinels. Here the magnetic entities are tetrahedral clusters and the magnetic moments depend on their local electronic structure. Depending on the number of valence electrons per cluster, compounds show diamagnetism as in Mo₄S₄I₄, paramagnetism as in GaNb₄X₈ and GaTa₄X₈, or Curie–Weiss behaviour and ferromagnetism below 25 K as in GaMo₄X₈ and the V compounds of the present study [5, 6]. The low-temperature magnetic and specific-heat properties of GaMo₄X₈ compounds could be analysed using the Stoner–Wohlfarth model and it was inferred that Mo₄ cluster electrons form a very narrow band at the Fermi energy [7]. The objection to this model has been the absence of metallic conduction at low temperatures. An alternative interpretation of the magnetic properties of these compounds has been proposed [4].

The difficulty in the study of the transport properties of these materials is mostly due to the poor sintering quality of these materials. During the course of synthesis of various cluster compounds, we found that V compounds are easily prepared as single phases and have better sintering quality. In this study we report electrical resistance, Seebeck coefficient and low-temperature AC conductivity measurements on V_4 compounds prepared under different conditions.

2. Experimental details

The compounds were prepared from the reaction mixture of powder elements in evacuated quartz tubes. The final temperatures of sintering of pressed pellets were 950 °C and 650 °C for 2 days for sulphides and selenides, respectively. The samples were either slowly cooled (GaV_4S_8 (I)) or rapidly quenched (GaV_4S_8 (II) and $Ga_{1.33}V_4S_8$) in water from 950 °C. The x-ray diffraction patterns reveal a single-phase compositions of the sulphides, in comparison with the reported x-ray measurements giving a wide homogeneity range of $Ga_xV_4S_8$. For the selenide composition, a temperature in excess of 700 °C gave the metallic phases of V selenides. The Seebeck coefficient and two-probe resistance measurements were made together in a closed-cycle refrigerator from 20 to 350 K. The samples in the shape of a disc of 1 cm diameter and 1–2 mm thickness were pressed between two copper stubs and a temperature gradient was established across the sample thickness. The differential temperature (1–5 K) was read from an Au–0.07% Fe-chromel thermocouple near the sample faces. The Seebeck coefficient was found from the slope of the thermovoltage versus differential temperature plot. It was found that the thermovoltage is sensitive to adsorbed gases and moisture at room temperature. The reported measurements were carried out after heating and evacuating ($\sim 10^{-4}$ mm) the sample in the cryostat at 150 °C. A separate four-probe arrangement for resistance measurements on the same sample over the range 20–350 K showed that the corrections for contacts and leads in two-probe resistances are not more than 5 Ω over the entire temperature range.

For the measurement of AC conductivity, we use the parallel plate capacitance geometry. For this, thin aluminized Mylar electrodes were attached against the disc faces with a fine layer of conducting silver paint, avoiding its seepage through the body of the sample. The complex impedance of the sample capacitor was measured using a four-terminal pair configuration in a closed-cycle refrigerator. The measurement contacts, using four coaxial cables, were made very near to the sample, and the sample capacitance to earth was minimized by an adequate earthing procedure. The complex impedance between 400 Hz and 200 kHz was measured using an HP4284A LCR bridge and all the needed corrections for stray impedances were incorporated into the final results.

3. Results

3.1. X-ray diffraction

All the compounds of this study gave diffraction peaks at 200, 420 and 640, consistent with the lowering of the space group symmetry of the spinels from the $Fd\bar{3}m$ to $F\bar{4}3m$ due to Ga-vacancy ordering on tetrahedral sites as found in the previous study of the Mo_4 cluster compounds [1]. Our data were not sufficient to find atomic positions from the x-ray peak intensities. The similarity of x-ray pattern, magnetic properties and low-temperature structural transitions with Mo_4 cluster compounds can be used to infer a similar V clustering

in our compounds. In table 1 we present the unit-cell parameters and I_{200}/I_{220} ratio, the peak intensity ratio being used to quantify the 1:1 order of Ga and vacancies. We find that the slow cooling of the compound $GaV_4S_8(I)$ gives more ordering compared to $GaV_4S_8(II)$ quenched from 950°C. There is also a net contraction of the lattice for samples containing excess Ga.

Table 1.

Compound	Unit cell		E_a^p (290 K)	E_a^s (290 K)
	a (Å)	$\frac{I_{200}}{I_{220}}$	(eV)	(eV)
$GaV_4S_8(I)$	9.64 ₅	2.8	0.14	0.1 ± 0.02
$GaV_4S_8(II)$	9.65 ₆	1.37	0.14 ₅	0.15 ± 0.02
$Ga_{1.33}V_4S_8$	9.60	1.27	0.145	0.04 ± 0.01
GaV_4S_7Se	9.74	2.0	0.135	0.04 ± 0.01
GaV_4Se_8	9.73	2.30	0.08	0.065 ± 0.01

3.2. DC resistivity

In figure 1, we present the temperature dependence of the resistivity of different $Ga_xV_4S_8$ compounds. Activated conduction is observed for all of them. The activation energy E_a^p estimated at room temperature to be 0.13–0.15 eV changes little for different samples of sulphide. The selenide compound gave a lower activation (0.08 eV) than the sulphides. The significant feature of our resistivity result is the observation of a continuous downward curvature in the plot for stoichiometric phases over a wide temperature range. The Se substitution of S and the compounds containing excess Ga gave a linear Arrhenius plot over the same temperature region. We also observe an AC resistance anomaly in GaV_4X_8 around the 45–50 K range. This may be due to a structural phase transition from cubic to rhombohedral distortion at lower temperature, similar to that observed in Mo_4 cluster compounds [4]. The magnetic susceptibility of GaV_4X_8 is also reported to show a sharp discontinuous increase below this temperature as in Mo_4 cluster compounds [5, 8].

3.3. Thermoelectric power

The mobility and sign of the charge carriers in our compounds could not be determined from the Hall coefficient measurements because of the very small values of the coefficient at room temperature. An upper limit of Hall mobility less than $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature could be estimated from the sensitivity of our measurements. The Seebeck coefficient shown in figure 2 could however be measured down to 80 K; at lower temperatures, the resistances of some samples became too large to give accurate values of Seebeck coefficient.

We find a limited range of $1/T$ behaviour in the thermopower of cluster compounds. The activation energies E_a^s estimated from $S = k_B/e[E_a^s/k_B T + \text{constant}]$ are listed in table 1. For stoichiometric and better-ordered $GaV_4S_8(I)$, the thermopower is negative with an $E_a^s = 0.1$ eV near room temperature. The quenching of sample II and 33% excess Ga concentration changes the thermopower substantially, the latter giving a positive Seebeck coefficient at low temperature. We find that in spite of differences in overall behaviour, the thermopower of all the compounds passes through a broad maximum in about the 150–200 K range and drops rapidly at lower temperatures.

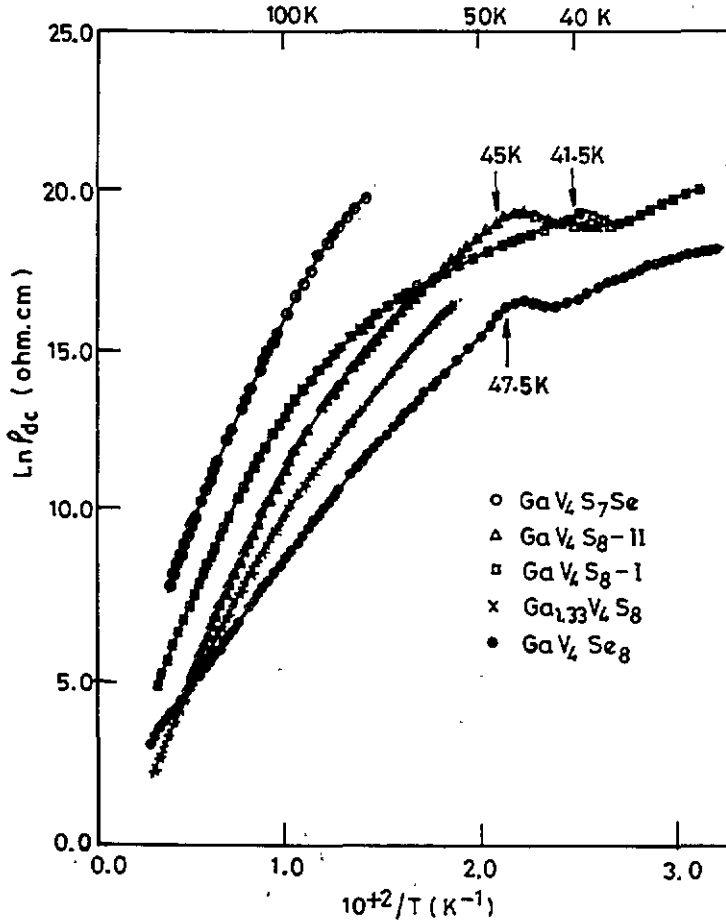


Figure 1. Arrhenius plot of resistivities of different V_4 -cluster compounds. The bumps correspond to structural phase transitions.

3.4. AC conductivity

The AC conductivity of GaV_4S_8 between 13 K and 100 K, measured by the capacitance loss method at a frequency of 7 kHz, is shown in figure 3. Except for an anomaly at 42 K associated with the structural phase transition, a non-linear Arrhenius plot is obtained over the full temperature range of measurements. The temperature-dependent activation energy obtained by the plot is shown in the inset. It is interesting to note that E_a^p thus obtained extrapolates to zero at 15 K, which is the ferromagnetic transition temperature reported in earlier studies [5, 8].

In figure 4 we plot $\sigma_{AC}(\omega)$ between 400 Hz and 200 kHz at different temperatures. We note that the transition at 42 K has little effect on the $\sigma_{AC}(\omega)$ behaviour since similar variations are obtained above and below the structural transition. The $\sigma_{AC}(\omega)$ of GaV_4S_8 look similar to that observed in a variety of amorphous solids and doped compensated semiconductors at low temperatures, where the increase in conductivity with frequency is a consequence of disorder, permitting conduction through well connected smaller clusters of sites during a half cycle of excitation with increasing frequency. In contrast, we observe such behaviour of $\sigma_{AC}(\omega)$ in compounds having a well ordered crystal structure and with no

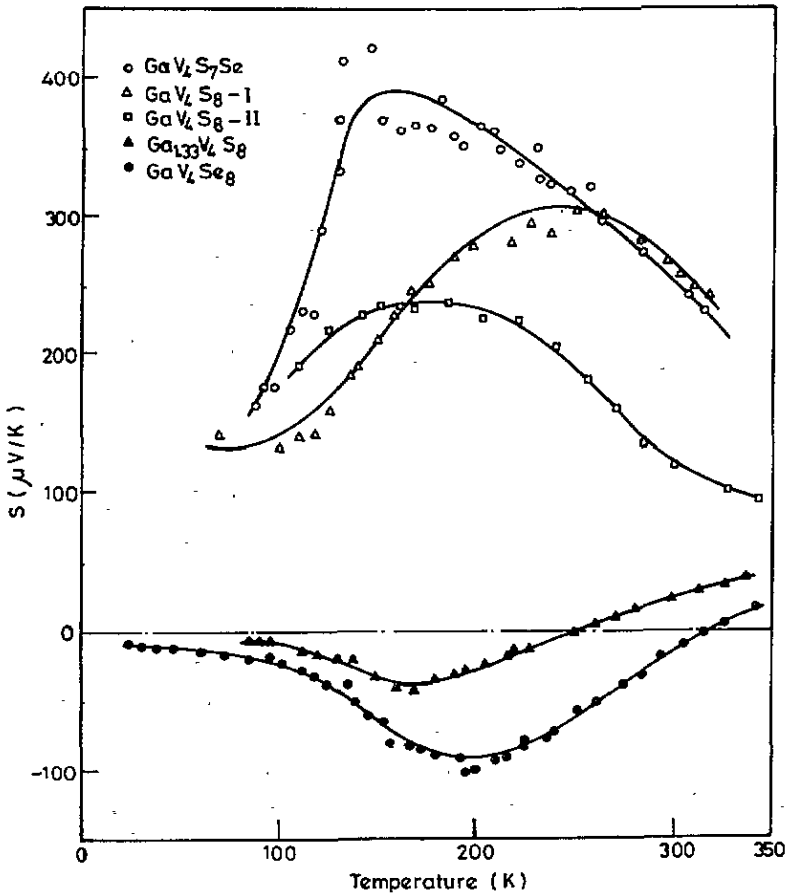


Figure 2. Thermopower against temperature of different V_4 -cluster compounds. All the curves show broad maxima in the 200 K range.

added impurity centres. In fact, the compound containing substituted Se, GaV_4S_7Se , was found to give much lower value of $\sigma_{AC}(\omega)$ in the same temperature and frequency range. The other important feature of $\sigma_{AC}(\omega)$ is that even at 50 K, a DC limit of conductivity could not be obtained at a frequency of 400 Hz indicating large relaxation times for the charge carriers in GaV_4S_8 . At low temperature, $\sigma_{AC}(\omega)$ follows ω^s with s tending to 0.8 as expected for hopping motion of carriers between pairs of localized sites [9].

4. Discussion

The main results of our measurements are (i) a continuous reduction of E_a^0 for electrical conduction with temperature, (ii) the departure of thermopower behaviour from wide-band conduction at low and intermediate temperatures and, most significantly, (iii) the observation of $\sigma_{AC}(\omega) = \omega^s$ with $s = 0.3-0.8$ between 20 K and 50 K in a well ordered stoichiometric V_4 -cluster compound. These are the familiar transport properties of doped-compensated semiconductors at low temperatures due to hopping motion of localized carriers on the random impurity centres. In our compounds these properties can be reconciled with the

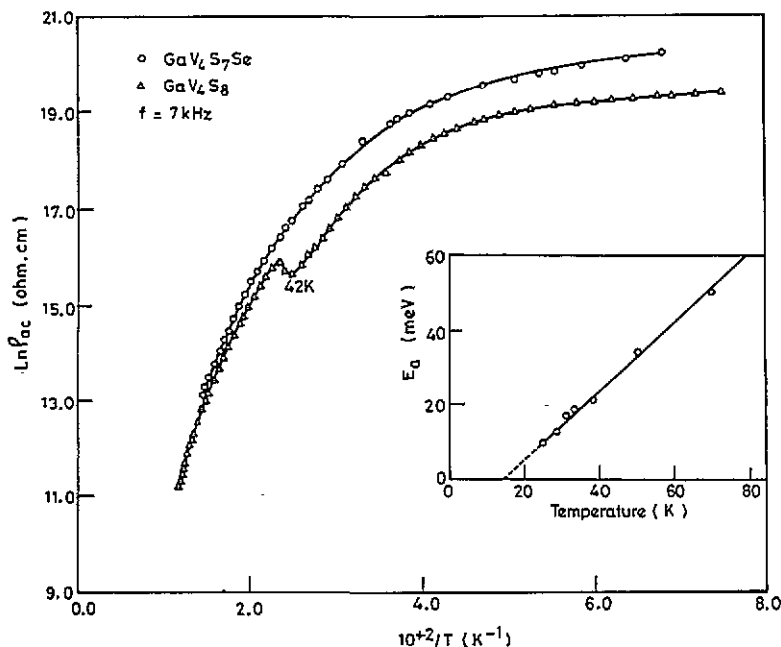


Figure 3. Arrhenius plot of the low-temperature part of the AC resistivity of $\text{GaV}_4\text{S}_8(\text{I})$ and $\text{GaV}_4\text{S}_7\text{Se}$ at 7 kHz. The inset shows the variation of activation energy with temperature.

localization of carriers similar to that proposed for spinel Fe_3O_4 and rutile Ti_4O_7 etc [10]. In the latter compounds charge carriers are heavy particles (charge polarons) localized on Fe^{2+} or Ti^{3+} lattice sites, which move by hopping to crystallographically equivalent Fe^{3+} or Ti^{4+} sites respectively. Such a state of the degenerate electron system has been termed Fermi glass or Wigner glass. When the ratio of the numbers of sites and charge carriers in these compounds is made non-integral by atomic substitution, i.e., it deviates from two, the long-range charge ordering and thus insulating phase is suppressed at low temperature. The transport properties are then those of a Fermi glass down to low temperatures. In a Fermi glass the density of states at the Fermi level remains finite and the glassy dynamics of carriers is a consequence of Anderson localization due to disorder in the carrier occupancy. Here, the main difference from the impurity conduction in Si is that the randomness in potential at a site is primarily due to long-range fluctuations in Coulomb field produced by the carriers on the wrong sites rather than due to randomness in intersite overlap integral. In this situation simultaneous multielectron hopping of carriers at low temperature gives an effective reduction in E_a^p . Because of the Coulomb repulsion among carriers and the degeneracy of carriers, the thermopower here is expected to deviate from Heike's expression at high temperature and should tend to zero as $T^{1/2}$ at low temperatures [10].

The ionic states of V in stoichiometric GaV_4S_8 would be 3V^{3+} and 1V^{4+} , akin to 25% compensation of doped impurity in semiconductors, except that in our compounds these states are intrinsic in nature and in much larger concentration. However, because of metallic bonding among the V_4 clusters it is not certain that these states of V ions have any meaning. On the other hand, as already mentioned, in GaV_4S_8 intercluster distances are quite large ($> 4 \text{ \AA}$) and so the band width of d electrons and the kinetic energy of carriers is expected to be small. A large intersite Coulomb repulsion and small overlap integral in crystalline phases would normally result in the ordering of heavy particles

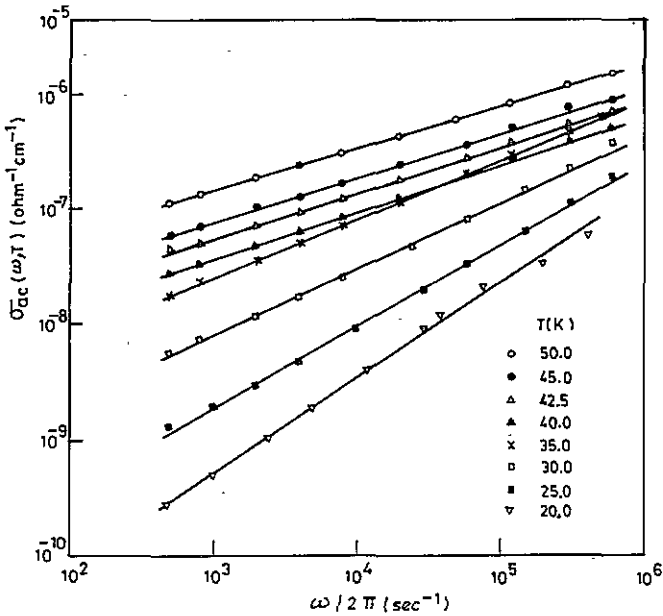


Figure 4. AC conductivity against frequency at low temperatures for $GaV_4S_8(I)$. $\sigma_{AC} \approx \omega^s$ where $s = 0.3-0.8$ between 50 K and 20 K.

and an insulating phase at low temperature [11]. However, as pointed out by Anderson, especially in the spinel structure, a random element of only 10% in the potential energy at a site due to only electrostatic forces is sufficient to suppress crystallization of carriers (*Wigner crystal*) and instead leads to the *Fermi glass state with the transport properties* mentioned above. In V_4 spinels the condition of Anderson localization would result from the small intercluster overlap and disorder potential due to incomplete Ga-vacancy ordering in $F\bar{4}3m$ space symmetry. It is pertinent to note that in the thiospinels of chromium such as $CdCr_2S_4$ where no B-atom clustering occurs, the Hall coefficient and thermopower measurements indicate a band motion of charge carriers with comparatively high mobilities for the transition-metal compounds [12].

The tetrahedral clustering results in the separation of six nearest-neighbour distances of B sites of the spinel into three short intra-cluster distances and three long inter-cluster distances, giving the cluster lattice of GaV_4S_8 the symmetry of NaCl structure with twelve-neighbour clusters. Under the integral occupancy of each cluster the effective valency of V is 3.25. During the hopping of carriers the effective valency of a V atom changes from +3 for occupied- to +3.5 for empty-cluster atoms. For the crystalline lattice these states form energy bands. However as mentioned earlier all the states in the band are Anderson localized due to a small random element in the Hartree-Fock potential. The special feature of cluster compounds is the non-integral charge states of the V atoms. This will certainly give a smaller Coulomb field at a given site compared to the case of Fe_3O_4 etc. If the bandwidth ($2zt$, $z = 12$) due to intercluster overlap t is not too small, then the banding effects and consequent reduced electrostatic interactions will on one hand suppress the tendency to charge ordering, but possibly stabilize the Fermi glass state [12]. On the other hand, they promote the regime of multielectron hopping to higher temperatures, which we believe is the correct interpretation for the decreasing gap in the large temperature range seen in our experiments. It is important to realize that under Coulomb interactions among

carriers, Mott's variable-range hopping for non-activated conduction is accompanied by variable-number hopping, of either cascade-like successive small hops, or, as Mott believes, a hop of an electronic polaron, wherein a long hop is accompanied by short hops of many electrons at the end points of motion. There may be other varieties of multielectron hopping. In all these models of multielectron hopping the activation energy is lowered with decreasing temperature giving $\ln \sigma \simeq B/T^n$ with $n < 1$. The value of n depends on the temperature, the nature of the Coulomb gap and the relative importance of disorder energy [13].

We now wish to examine our results for polaronic effects. For this it is relevant to consider activation energies seen in DC conduction and thermoelectric power. The activation energies E_a^p and E_a^s at 290 K for the samples of study are listed in table 1. We find that E_a^s for different sulphides is the same irrespective of lattice constant and externally induced defects. This would suggest a relatively minor contribution of polaron energy W to the activation in the mobility of carriers and conduction in a wider band of localized states, since otherwise changes in intercluster overlap due to lattice contraction would result in an exponential change in hopping mobility. The weak polaron effect is also supported by the close values of E_a^p and E_a^s in stoichiometric GaV_4S_8 . The observed difference $E_a^p - E_a^s$ in $\text{Ga}_{1.33}\text{V}_4\text{S}_8$ cannot be attributed to the activated mobility of polaron hopping, since here thermopower changes sign at low temperatures. This would rather suggest a mixed nature of conduction in the doped specimen; the negative thermovoltage is compensated by the holes in the band. The absence of polaronic distortion of lattice and the mechanism of localization in the narrow band of the V thiospinel is to be contrasted with the mechanism of localization proposed for oxide spinels of $\text{V Mg}_{1-x}\text{Li}_x\text{V}_2\text{O}_4$. In the latter, polarons are formed by doping of carriers in V bands and the thermopower above 200 K obeys Heike's formulation of a non-degenerate gas of polarons in a band with the bandwidth less than $k_B T$ [14].

In the theory of conduction among localized states the activation energy E_a at high temperature is related to the average Coulomb interaction between occupied near-neighbour sites. During the hopping process an electron is thermally activated to the Fermi level, thus enabling the neighbouring electrons to move in. For strong localization, all the states in the band participate in conduction and $E_a = Ce^2/\kappa a$, where $C < 1$ is related to the distribution of charges which give dispersion to the energy levels. For GaV_4S_8 , $E_a = 0.14$ eV, intercluster hopping distance $a = 6.8 \times 10^{-8}$ cm using the NaCl-type V_4 sublattice, and taking $C = 0.3$ would give a reasonable value of dielectric constant $\kappa = 4.5$ similar to that in other inorganic sulphides. The value of C has been taken from the study of the measured variation of the activation energy of impurity conduction in 30% compensated p-type Ge [15].

We would now like to demonstrate the consistency of our picture of Fermi-glass-like conduction by estimating a few parameters numerically. In particular we show that the measured value of E_a is consistent with other Fermi-glass parameters. For this purpose, we note that according to Mott, the DC conductivity of a Fermi glass obeys the behaviour $\sigma_{\text{DC}} = A \exp[-(T_0/T)^{1/4}]$ where A is a temperature-dependent prefactor (temperature dependence arising due to correlation effects) and $T_0 = \beta/[k_B \alpha^3 N(\epsilon_F)]$. Here β is determined by arguments of percolation theory to be 13.8 ± 0.8 , α is the localization radius of the states near the Fermi level and $N(\epsilon_F)$ is the density of states at the Fermi level. Thus a knowledge of T_0 would permit an estimation of $N(\epsilon_F)$. In order to obtain T_0 , we use our AC conductivity data between 20 and 40 K as shown in figure 3 and figure 4. T_0 cannot be determined by taking the $\omega \rightarrow 0$ limit, as this limit is non-analytical. It may also be seen that the temperature-dependent activation energy $E_a(T)$ shown in the inset of figure 3 deviates from $T^{3/4}$ variation as expected from Mott's analysis. Such a behaviour is quite normal for

a Fermi glass with a wide spread of transition rates. So we follow the scaling analysis given by Hunt [16]. Detailed results using this analysis will be presented in a future publication. For the present we note that our $\sigma_{AC}(\omega, T)$ results can be scaled in the temperature range 20–40 K to a universal curve $\sigma_{AC}(\omega, T)/\sigma_{AC}(0, T) = f(\omega/\omega_c)$, where the scaling frequency $\omega_c = \omega_{ph} \exp[-(T_0/T)^{1/4}]$; ω_{ph} is a temperature-independent factor. The values of ω_{ph} and T_0 are found to be $\omega_{ph} = 10^{10.5} \text{ s}^{-1}$ and $T_0 = 1.8 \times 10^5 \text{ K}$. Using this value of T_0 and taking α to be half the intercluster distance, we find $N(\epsilon_F) \simeq 4.8 \text{ states eV}^{-1}/\text{formula unit}$. Now if each cluster contributes one state to the band around the Fermi level, and for a uniform density of states, the bandwidth turns out to be 0.2 eV, which is rather close to the activation energy $E_a = 0.14 \text{ eV}$ observed in our compounds. Considering the crudeness of our approximations for the density of states, localization radius etc., this is an encouraging result towards the interpretation given above.

5. Conclusions

Although structural and magnetic properties of chalcogenides containing transition-metal clusters V_4 , Mo_4 , Nb_4 etc have been known for about two decades, the study of their transport properties have rarely been undertaken. We have reported conductivity and thermopower measurements on ferromagnetic semiconductors GaV_4S_8 containing V_4 tetrahedral clusters. The significant observation is the Fermi-glass behaviour in their stoichiometric phases. This is in contrast with the wide-band semiconduction of the magnetic spinel $CdCr_2S_4$ etc and is mainly due to large intercluster separation in our compounds. The realization of Anderson localization of cluster electrons is a consequence of random Hartree-Fock potential from the Ga-vacancy disordering. Because of a narrow band and high concentration of sites, the electron-electron interaction effects will dominate the hopping process over wide temperature ranges. We believe that the observed reduction in E_a^p over a large temperature range is the result of multielectron (correlated) hopping of carriers. The most encouraging result of our analysis is that the parameter T_0 obtained from $\sigma_{AC}(\omega, T)$ using Hunt's theory for variable-range hopping gives a bandwidth consistent with the value of E_a , the high temperature activation energy of GaV_4S_8 . This leads us to conclude that the density of states at the Fermi level is non-zero and conduction is among the localized states, i.e. GaV_4S_8 is a Fermi glass. This observation will help in clarifying some of the interesting magnetic and specific-heat properties reported for the transition-metal cluster compounds, particularly those containing Mo_4 clusters [7].

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