Structural and electronic properties of the Nb$_4$-cluster compound Ga$_{1.33}$Nb$_4$X$_8$ (X = S, Se)

Asad Niazi$^1$ and A. K. Rastogi$^2$

$^1$ Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai - 400005, India
$^2$ School of Physical Sciences, Jawaharlal Nehru University, New Delhi - 110067, India

We report resistivity, thermopower and magnetic susceptibility measurements on the Nb$_4$-cluster compounds Ga$_{1.33}$Nb$_4$X$_8$ (X = S, Se), derived from vacancy ordered spinels A$_x$T$_4$X$_8$. The cubic selenide phase is insulating and its resistivity crosses over from $\ln \rho \sim T^{-1}$ to $\sim T^{-1/2}$ on cooling below 150 K, indicating variable range hopping (VRH) conduction at low temperatures. This is similar to that previously reported for V$_4$ and Mo$_4$ cluster compounds. The rhombohedrally distorted sulfide is metallic and shows a minimum in resistance at $\sim 56$ K below which the resistivity varies as $\rho(T) \sim T^{-1/2}$. The thermopower of the selenide becomes temperature independent below the crossover temperature. These Nb$_4$ compounds exhibit enhanced Pauli-paramagnetic magnetic susceptibility ($\chi$) irrespective of their transport properties and both undergo a similar transition in $\chi(T) \sim 30$ K. We discuss these properties in the model of hopping conduction under long-range Coulomb repulsion effects and derive consistency between some of the transport and magnetic parameters.

70.,72.20Ee,72.80.Ga,75.20.-g

I. INTRODUCTION

Cation rich compounds of the early transition metals, especially the 4d and 5d chalcogenides, show large clustering of the metal sublattice with groups of metallic-bonded atoms separated by large intercluster distances. These structural features remarkably increase electronic correlations and lead to a variety of phase transitions at low temperatures. Of special interest are compositions such as AT$_6$X$_8$ and AT$_4$X$_8$, where high-symmetry cubic and hexagonal-rhombohedral structures are obtained and the cluster disorder is expected to be small. The metallic phases of Mo$_6$ and Rh$_4$ have been found to be superconducting, the $T_c$ increasing with intercluster distances. The superconducting parameters suggest a highly localised wavefunction on the atomic clusters. For still larger intercluster distances such as in V$_4$, Nb$_4$ and Mo$_4$ compounds, the transport properties are found to be dominated by Coulomb and exchange interaction effects among cluster electrons, as even a small disorder in the lattice potential gives a localised electron glass state. They also become magnetic below about 30 K. The compounds of the present study belong to the same family and are expected to show smaller correlation effects compared to V$_4$ and Mo$_4$.

All the compounds AT$_8$X$_8$ (A = Ga, Al; T = V, Nb, Ta, Cr and Mo; X = S, Se, Te; space group $F\bar{T}d_3m$) are insulating and are derived from spinels AB$_2$O$_4$ (space group $Fd\bar{3}m$) with vacancy ordering at the A-sites and metal-clustering ($T_4$) of B-site cations. The dominating effect of metal clustering on the electronic properties is seen in the remarkably similar transport and magnetic properties among the compounds of V$_4$ and Mo$_4$ belonging to the 3d and 4d series respectively. The magnetic properties of Nb$_4$, Ta$_4$ and mixed Nb$_4$-Mo$_4$ compounds have been reported in a previous study. The large Pauli-paramagnetism measured in Nb$_4$ suggested a partially occupied, although localised electronic band of states at the Fermi-energy ($E_F$). Recent band structure calculations on V$_4$ and Mo$_4$ compounds also gave a partially empty and very narrow d-band at $E_F$ which is in accord with their magnetic properties and the observed hopping conduction of carriers. The mechanism of electron localisation, however, remains unexplained.

In this paper we present the structural, transport and magnetic properties of Ga$_{1.33}$Nb$_4$S$_8$ and Ga$_{1.33}$Nb$_4$Se$_8$. While both these phases were previously reported to be cubic at room-temperature, our sulfide compound reported here is found to have rhombohedral symmetry and shows metallic conduction in contrast to insulating behaviour of the cubic phases. However, its lattice constants, the observed superstructural phases and the remarkable similarity in its magnetic properties with the cubic phase suggest important similarities in the short range atomic arrangements in the metallic and the insulating phases.

II. SYNTHESIS AND STRUCTURE

A series of Ga$_x$NbS$_2$ ($x = 0.1, 0.25, 0.33$) was prepared from the elements in sealed quartz tubing 5% excess sulfur at 850 °C (low temperature (LT) phase) and also above 1100 °C (high temperature (HT) phase). For the selenide the starting composition used for reaction of the elements was Ga$_{33}$NbSe$_2$ (+ 5% excess Se) and final sintering of pellets was done at 950 °C. Single crystal flakes could be obtained for 2H-NbS$_2$ and for 3R-Ga$_{1.33}$NbS$_2$. 

---

1Present Address: Dept. of Physics, Faculty of Natural Sciences, Jamia Millia Islamia, New Delhi 110025, India. Email: asad@jamia.net
2Email: ak@phy.jnu.ac.in
The details are given elsewhere [9].

A. 3R-Ga$_{33}$NbS$_2$ ($x = 0 - 0.33$)

Here we briefly review the properties of 3R-Ga$_{33}$NbS$_2$. Structurally, all these phases except for $x = 0.33$ (HT), are derived from an intercalated 3R-Nb$_{1+x}$S$_2$ ($x \leq 0.1$) host. The intercalated atoms occupy octahedral sites in the van der Waals gap giving a rhombohedral unit cell with $R3m$ symmetry. The transport properties of pressed sintered pellets and the flakes showed metallic behaviour and a resistance minimum between 20–60 K. The resistance minimum was related to the combined effects of increasing disorder and clustering interactions among in-plane Nb atoms [8].

For 33% Ga, the structure of the 1100 °C quenched HT phase was found to be markedly different from the LT phase prepared below 850 °C. This is evident on comparing their XRD patterns in Fig. 1(a) and (b). The structural parameters of the LT phase, $a_H = 3.34$ Å, $c_H = 7.90$ Å, are similar to the other Ga-intercalated NbS$_2$ compounds. However, there is a large increase in the number and intensity of the superstructural lines (marked by * in Fig. 1(a)) indicating increased clustering of Nb atoms in the $a$-$b$ plane. The HT phase has a qualitatively different structure. All the lines in the pattern can be indexed on a $2 \times 2$ hexagonal supercell, but with a substantially increased corresponding $c$-parameter of $2 \times 3.6$ Å. There is also a large reduction in its $c$-parameter to a value of 17.31 Å, making $c/a = 1.603$, as compared to $\sim 1.80$ for the rest of the compounds. The HT phase remains metallic in spite of these structural changes. However, as we later show, its magnetic properties are changed and become remarkably similar to the insulating phases of Nb$_4$-compounds, suggesting similar clustering in our HT phase.

The rhombohedral cell parameters ($a_R$, $\alpha$) of our HT phase and that of the cubic GaNb$_4$S$_8$ ($a_C = 10.02$ Å) reported earlier [8] are very similar, being (7.11 Å, 60.81°) and (7.085 Å, 60°) respectively. It is therefore worthwhile to compare other important features of rhombohedral layered CdCl$_2$ and cubic spinel structures from which our Ga$_{33}$NbS$_2$ and GaNb$_3$S$_8$ are respectively derived. In both cases the anions form a cubic packing. In CdCl$_2$, the transition metal atoms occupy all the intralayer-octahedral sites, which alternate with the intercalate atoms in the van der Waals gap. In spinels on the other hand, 1/4 of the transition metal atoms are transferred to the octahedral sites in the van der Waals gap so as to form (a) a $2 \times 2$ vacancy ordered supercell and (b) a tetrahedral arrangement of neighbouring transition metal atoms. The clustering interactions in our compounds give an f.c.c. lattice of well-separated T$_4$ clusters. We believe that in Ga$_{33}$NbS$_2$ this arrangement is obtained by high temperature synthesis. There may be differences in the site (tetrahedral/octahedral) occupancy of Ga atoms in these phases which can be resolved by EXAFS studies. We shall therefore, in the subsequent discussion represent 3R-Ga$_{33}$NbS$_2$ as Ga$_1$$_{33}$Nb$_4$S$_8$.

B. Ga$_{1.33}$Nb$_3$S$_8$ and Ga$_{1.33}$Nb$_4$Se$_8$

As mentioned above, high temperature synthesis of sulfides for 33% Ga gave a rhombohedrally distorted phase whose structure is quite similar to the previously reported cubic Nb$_4$-cluster compound. In contrast, the selenide compound was easily obtained with a cubic structure as can be seen from its XRD pattern reported in Fig. 1(c). The presence of (200), (420) and (600) lines indexed on an f.c.c. lattice ($a_C = 10.41$ Å) indicates the $Fm\overline{3}m$ space group. A detailed single crystal analysis of the cubic phases [8] had shown the existence of strong tetrahedral Nb$_4$-clustering. In common with the V$_4$ and Mo$_4$-cluster compounds, the intracluster distances were found to be 3.026 Å, similar to Nb metal, but large intercluster distances of 4.320 Å rendered these compounds insulating.

A note on polymorphism: The crystal chemistry of ternary chalcogenides of the early transition elements is dominated by CdI$_2$-NiAs-type covalent structures. There are only a few cubic thiospinels of Ti, V and Zr and they invariably contain Cu on tetrahedral sites. The existence of cubic structures for A$_2$TX$_2$ (A = Ga, Al, Cu; T = early transition element) seems to be intimately related to the extraordinary clustering of transition elements on the T-site. It should be noted that the more ionic compositions of late transition elements of the 3d series (Cr–Ni) can exist as cubic thiospinels as well as subtractive NiAs-type hexagonal modifications whether prepared synthetically or obtained as naturally occurring minerals. Polymorphic transformation to the latter variety is also obtained at high pressure and temperature when the A-site has unfilled orbitals or has equal preference for octahedral sites of the structure [10]. In our Ga$_2$Nb$_3$S$_8$ compounds too we observe similar structural modifications of phases upon using different methods for their synthesis. Similarly, in a recent study of Cu-substituted GaV$_4$S$_8$, cubic, hexagonal and orthorhombic structures were obtained using different methods of synthesis – from the elements and by reduction of oxides at different temperatures. The hexagonal phases were found to be metallic, while cubic phases showed insulating behaviour and interestingly the orthorhombic ones underwent metal to insulator transition below 180 K [11].

III. TRANSPORT PROPERTIES

A. Metallic Ga$_{1.33}$Nb$_3$S$_8$

The structural and magnetic properties of cubic (insulating) phases of Nb$_4$ compounds have been reported
previously [6]. We now compare the conductivity and thermopower measurements on pressed sintered pellets of HT and LT Ga$_{1.33}$Nb$_3$Se$_8$ in Fig. 3. Both these compounds show metallic behaviour on cooling and a resistance minimum respectively at about 40 K and 56 K. A distinct anomaly is also noticed in the thermopower below $T_{\text{min}}$ where a rapid drop from positive to negative value occurs. There is however a marked difference in the overall behaviour related to the increased atomic clustering in the HT phase.

The HT phase has larger resistivity, and it saturates and passes through a broad maximum above room temperature. On the other hand, the resistivity variation of the LT phase is quite similar to and properly scales with the variations found in the lower Ga-containing phases including 3R-Nb$_{1+x}$S$_2$, observed on plotting $\rho/\rho_{\text{min}}(T/T_{\text{min}})$ between $2 < T/T_{\text{min}} < 2$. This scaling is obtained for resistivity values differing by an order of magnitude. The changed $\rho(T)$ behaviour compared to the LT phase is certainly related to structural changes and significantly increased electron localisation upon metal-atom clustering in the HT phase.

The increase in carrier localisation can also be seen in the thermopower of the HT phase which remains independent of temperature above $T_{\text{min}}$, whereas in the LT phase there is rapid increase on heating. It is here significant to note that upon cooling below $T_{\text{min}}$ all the phases including Nb$_{1+x}$S$_2$ showed a similar changeover of $S$. The overall thermopower behaviour of these compounds is quite complicated and a satisfactory explanation of the different behaviour above $T_{\text{min}}$ cannot be provided. A temperature independent thermopower along with resistance maximum at high temperature is expected for polaronic transport. However, the band parameters and significant electron-electron interaction effects causing resistance minimum at low temperatures in these compounds are inconsistent with the simple model of non-degenerate gas of small polarons, as suggested for many doped transition metal oxides [12]. We, on the other hand, believe that in these cluster compounds the electronic properties are primarily related to the lattice disorder and strong correlation effects among the carriers.

## B. Insulating Ga$_{1.33}$Nb$_3$Se$_8$

As already mentioned, in common with the other tetrahedral cluster compounds, the cubic phase of our Ga$_{1.33}$Nb$_3$Se$_8$ is insulating. In Fig. 3(a) we show its resistivity behaviour between 40–500 K on a ln $\rho(1/T)$ plot. Figure 3(b) shows the thermopower behaviour between 50–300 K on a $S(1/T)$ plot. The thermopower changes sign from a negative value at room temperature to positive below 200 K. A general expression of diffusive thermopower, irrespective of the nature of conduction (band or hopping conduction), can be written as

$$S = -\frac{k_B}{|e|} \left( \frac{\langle \epsilon > - \mu}{k_B T} \right)$$

where $\langle \epsilon >$ is the average energy and $\mu$ is the chemical potential. For an extrinsic semiconductor, $(\langle \epsilon > - \mu)$ would represent the energy of carrier generation; and for band conduction similar slopes are obtained for $\ln \rho(1/T)$ and $S(1/T)$ plots. The results presented in Fig. 3 clearly show that the activation energy for electrical conduction is quite different from that observed in thermopower. The large difference in slope at high temperature cannot be accounted for by polaronic hopping. Moreover, there is a strong downward curvature in the resistivity plot while the thermopower becomes constant below 150 K. Thus, the activation energy reduces from $\sim 0.14$ eV at high temperature to just $\sim 0.026$ eV at 40 K. These results are qualitatively similar to those obtained earlier for the V$_4$ and Mo$_4$-cluster compounds [6].

We shall later analyse some of the results in the model of impurity band conduction in a semiconductor, where variable range hopping (VRH) observed at low temperatures has been extensively studied [12,13]. Moreover, as shown in the inset, the resistivity follows $\rho = \rho_0 \exp(T_0/T)^{1/2}$ below 150 K, while as mentioned above, the thermopower becomes nearly temperature independent. A value of $T_0 = 1.8 \times 10^4$ K is obtained from the plot. The $T^{1/2}$ dependence has been previously reported for the cluster compound GaMo$_3$Se$_4$Te$_4$ where a crossover from $\ln \rho \sim T^{-1/4}$ to $\ln \rho \sim T^{-1/2}$ was found below a similar temperature of 175 K. This behaviour was attributed to Coulomb repulsion effects on the VRH of carriers at low temperature. Taking into account the Coulomb gap effects near the $E_F$ of hopping carriers, Burns and Chaikin have earlier obtained an expression for $S$ that tends to a constant value at low temperatures [14].

## IV. MAGNETIC PROPERTIES

The magnetic properties of different cluster compounds of V$_4$, Nb$_4$, Ta$_4$ and Mo$_4$ have previously been reviewed [7]. The ferromagnetism in V$_4$ and Mo$_4$ compounds, which also show VRH conduction, had been discussed in the model of Anderson localised states by including on-site Coulomb repulsion and exchange interaction among singly occupied sites [8]. In the following we present paramagnetic properties of Ga$_{1.33}$Nb$_3$Se$_8$ and Ga$_{1.33}$Nb$_3$S$_8$.

In Fig. 4(a), we present the magnetic susceptibility ($\chi(T)$) results of Nb$_4$-compounds. Qualitatively similar behaviour on cooling, including a sharp reduction in $\chi$ around 30 K followed by a Curie tail can be seen in all of them including the metallic sulfide phase of the present study. The $\chi$ of the selenide is about twice the value of the sulfide indicating that the partially filled band has larger DOS($E_F$), principally due to larger intercluster distances in selenides. The susceptibility in these compounds should be compared to much weaker
paramagnetism as well as the absence of low temperature transition in Nb$_4$Se$_4$I$_4$ [7]. In this compound similar tetrahedral Nb$_4$ clusters are formed, but now eight valence electrons per cluster would correspond to a full $d$-sub band.

It is important to note that in Nb$_4$-cluster compounds, $\chi$ shows a fall below the transition whereas in V$_4$ and Mo$_4$ compounds the $\chi$ increases sharply below the transition around 45–55 K and they become ferromagnetic below 10–25 K. However, there is no qualitative difference in their transport properties as all of them show VRH conduction. The remarkable independence of magnetic properties from their transport behaviour is also seen in Fig. 1 where the metallic and insulating phases of sulfides are seen to have the same magnitude of $\chi$. We also note that in the metallic phase, except for a minimum at a higher temperature of 56 K, no visible anomaly is noticed in the resistance corresponding to the sharp decrease in $\chi$ below 30 K. In earlier studies, $\chi$ and Mo$_4$ compounds also showed only a weak cusp in ac and dc-resistance in their ln $\rho$ vs $1/T$ plots around 45–55 K corresponding to the transition in $\chi$ [3,4]. Similar studies for the transport properties of our insulating Ga$_{1.33}$Nb$_4$Se$_8$ could be not be made since its dc-resistance became very large below 40 K.

The $\chi(T)$ in all the Nb$_4$-compounds showed a Curie tail at low temperatures. In the inset of Fig. 1, we have shown $M(H)$ plots of metallic Ga$_{1.33}$Nb$_4$S$_8$ and insulating Ga$_{1.33}$Nb$_4$Se$_8$ at 2 K up to 120 kOe field. Both show a characteristic curvature and a linear slope, indicative of localised moments ($x$/mole) and high field Pauli-paramagnetic contribution ($\chi_HF$) respectively. In the main figure we have replotted the local moment contribution and compared it to a Langevin function for spin $1/2$ moments for both the compounds. This simple analysis gives the following parameters : $x = 1.02 \times 10^{-2}$ and $1.91 \times 10^{-2}$/mole and $\chi_HF = 1.74 \times 10^{-3}$ and $3.86 \times 10^{-3}$ emu/mole respectively for Ga$_{1.33}$Nb$_4$S$_8$ and Ga$_{1.33}$Nb$_4$Se$_8$.

The values of $x$ obtained above from the saturated spin-$1/2$ moments give Curie constants equal to $3.83 \times 10^{-3}$, $7.16 \times 10^{-3}$ respectively for the sulfide and selenide. These values are used to subtract the Curie contribution from the $\chi(T)$ results of Fig. 1 and the susceptibility is plotted in Fig. 3. It is uncertain whether a sharp change in $\chi(T)$ below 6 K is an artifact of our subtraction procedure or an intrinsic property of these compounds. Apart from this, the results obtained are very similar to those reported earlier for the Nb$_4$ compounds. The value of $x \sim 0.01$ in these phases is sufficiently large not to be attributed to extrinsic magnetic impurities. Rather, these localised moments seem to be related to the local changes in the Nb$_4$-lattice arising from non-stoichiometry. This conclusion is in accord with the results on mixed clusters of Nb-Mo, where the Curie constant reduces from the spin-$1/2$ per cluster in Mo$_4$ to about 1–2% of the value in Nb$_4$-compounds. It is significant to note that while V$_4$ and Mo$_4$ compounds showed a large increase in $\chi(T)$ at 45–55K, Nb$_4$ compounds showed a drop around 30 K. The reason for this difference is not clear at the moment.

V. DISCUSSION

The most significant result of the present study is the synthesis of a rhombohedral Ga$_{1.33}$Nb$_4$S$_8$ phase which is found to be metallic, while the cubic phases of GaNb$_4$S$_8$, GaNb$_4$S$_8$ and Ga$_{1.33}$Nb$_4$Se$_8$ are insulating. There is however remarkable similarity in their magnetic properties. The change to metallic behavior cannot be simply related to carrier doping by impurity atoms as in a wide band semiconductor. The occurrence of metallic conduction in a rhombohedrally distorted Nb$_4$ compound clearly suggests important changes in band-dispersion due to cluster distortion and consequently in the condition for Anderson-localisation of the wave-function. The disorder effects, however, remain significant as seen from the $R(T)$ and $S(T)$ anomalies in the metallic phase. The observed $\sigma(T) \sim T^{1/2}$ below $T_{\text{min}}$ has been related to the Coulomb gap corrections to the DOS in disordered solids as suggested by Altshuler and Aronov [7]. In the cubic phases of Nb$_4$, V$_4$ and Mo$_4$, the transport and magnetic properties are also insensitive to the changes in concentration or substitution of Ga or Al by Cu, Zn, etc.. This insensitivity to carrier doping indicates that in cluster compounds the Fermi level is pinned to a band of states. The states are localised due to disorder and correlation effects and conduction is by phonon assisted hopping of carriers. A survey of the high temperature activation energy ($\epsilon_F/k_B$) for different sulfides, selenides and tellurides of cluster-compounds gives values between 700–1800 K. The highest for GaV$_4$S$_8$ and lowest for GaMo$_4$Se$_4$Te$_4$ [3]. These observations indicate that the localisation of the wavefunction of cluster electrons has similar origin for different transition metal atom clusters. All the insulating compounds show strong downward curvature in the ln $\rho(1/T)$ plots, which is characteristic of Mott’s VRH conduction. In some cases Coulomb repulsion effects on the hopping carriers give a changeover to $\rho = \rho_0 \exp (T_c/T)^{1/2}$ behavior at low temperature, as we have reported above for Ga$_{1.33}$Nb$_4$Se$_8$ below 200 K.

For cubic structures, recent electronic energy calculations based on Density Functional Theory within a local density approximation clearly show that the ideal thiospinel structures of these compounds are metallic and that there is substantial effect of atomic clustering on the band energies near the Fermi level of $t_d$ orbitals of transition elements, and upon their clustering there appears a gap $\sim 1.4$ eV above the occupied band. Surprisingly, the Fermi level now remains in a much narrower lower $d$-band leaving hole-like states just below the band-gap. The wavefunctions of these empty states are expected to be drastically modified by subtle electronic correlations and also by small atomic disorder in actual compounds,
leading to Mott’s metal-insulator (M-I) transition. The DOS($E_F$) for different compounds of V$_4$ and Mo$_4$ is calculated to be substantially high and varies between 10–20 states/eV/F.U. [8]. Qualitatively similar conclusions about high DOS($E_F$) were drawn from the detailed analysis of low temperature magnetic, specific heat and transport properties [12].

We observe a similarity of transport properties, especially the crossover to $\ln \rho \sim T^{-1/2}$ behavior below 200 K for Ga$_{1.33}$Nb$_4$Se$_8$, with GaMo$_4$Se$_4$Te$_4$ reported earlier [5]. This shows the importance of correlation effects due to Coulomb repulsion among hopping electrons as suggested for the impurity doped, moderately compensated semiconductors [3]. A detailed analysis of the transport and magnetic parameters using a similar model will be reported in future. In the following analysis we try to check the consistency of parameters in the above model. For Ga$_{1.33}$Nb$_4$Se$_8$, $\epsilon_3/k_B = 1700$ K, Shklovskii parameter $T_\alpha = 1.85 \times 10^4$ K and $\chi_{300} = 12 \times 10^{-4}$ emu/mol.

We should note that for our cluster-compounds the suitability of the model for hopping conduction among widely separated impurity centers in a lightly doped-compensated Si or Ge semiconductors rests on the important observation by Hill that, for a wide variety of solids showing VRH, the normalised site density, $N = N_1/\alpha^{-1}$ ($N_1 = $ density of sites and $\alpha^{-1} = $ localisation length of carriers) falls within a narrow range of 0.1–0.14 [3]. In our cluster compounds this condition seems to be satisfied even under a high density of carriers.

For impurity bands a random electrostatic potential originates from fixed complexes of ionised donors and acceptor impurities. This gives a dispersion of band energy of the impurity states around a maximum which is located near the energy of non-ionised donors. The DOS falls to zero within the characteristic ionisation energy of donors. The chemical potential ($E_F$), calculated for lightly compensated impurities, is found at an energy $E_F = 0.61 \epsilon_D$ away from the maximum; where $\epsilon_D = e^2/\kappa r_d$, $\kappa = $ dielectric constant and $r_d$ the average separation of donors, [3]. For nearest neighbour hopping at high temperatures the conductivity is due to ionisation of donors located near the maximum of DOS. Thus a constant activation energy is obtained, given by

$$\epsilon_3 = E_F = .61 \epsilon_D. \quad (2)$$

In case of our cluster compounds, similar compensation effects can originate from the Ga atoms occupying tetrahedral sites and may also contribute the needed random potential for the dispersion of band energies. In this context, it is important to recall that here the tetrahedral sites of spinels are only partially occupied and occupancy disorder may be significant enough to cause localisation of cluster electrons.

At low temperatures, hopping is among impurities having their energies near the Fermi level, and Mott’s VRH is obtained for a flat DOS. However, the electronic correlations will modify DOS and hence hopping conduction. A qualitative estimate of $g(E_F)$ can be made in case of low compensation. The DOS falls off to zero within $\epsilon_D$ and the empty states in the band should correspond to the density of compensating impurities, thus giving $N_a \sim \frac{1}{2}g(E_F)\epsilon_D$, i.e. $g(E_F) \sim 2N_a/\epsilon_D$.

Various studies on the effect of long range Coulomb interaction between hopping electrons have shown that the single particle DOS vanishes at $E_F$ with a soft gap $\Delta$. This so called Coulomb gap has important effects on the conduction below a temperature $\Delta/k_B$, where for hopping in 3-dim, Mott’s $\ln \rho \sim T^{-1/2}$ is replaced by $\sim (T_\alpha/T)^{-1/2}$ dependence. The following expressions have been derived in case of doped-compensated semiconductors by Efros and Shklovskii [13]:

$$k_B T_\alpha = 2.8\epsilon^2/\kappa \alpha^{-1}, \quad (3)$$

$$\Delta^{2/3} = \epsilon_D[r_d g(E_F)^{1/3}]. \quad (4)$$

Let us now apply these relations in case of Ga$_{1.33}$Nb$_4$Se$_8$. The observed activation of 1700 K around room temperature and intercluster distance of 4.3 Å for Nb atoms would require a dielectric constant $\kappa = 14$ from relation (3). This value of $\kappa$ should be compared with about 25 expected for Se$^{2-}$ ions. In another way the parameter $e/\sqrt{\kappa}$ in (3) can be thought of as effective charge of the hopping carriers. Using $N_a$ as the Ga concentration, we obtain $g(E_F) = 8.5$ states/eV/F.U.. This value should be compared with the band structure calculations of 10–20 states/eV/F.U. for various cluster compounds [3]. The expected magnetic susceptibility is therefore $\sim 1.4 \times 10^{-4}$ emu/mol. The observed value of $6 \times 10^{-4}$ at 300 K for our Nb$_4$ compound shows a significant exchange enhanced paramagnetism. The compounds of V$_4$ and Mo$_4$ become magnetic due to much larger exchange correlation among the clustered electrons [17]. Using relation (3), the Efros-Shklovskii parameter $T_\alpha$ can be used to calculate the localisation length $\alpha^{-1}$ which equals about 1.8 Å. However, relation (4) for the Coulomb gap does not seem to give the observed crossover temperature of about 200 K, as we obtain a value larger by an order of magnitude. This in our opinion is quite significant and certainly indicates a different nature of correlated hopping in these compounds. It should be remembered that the above model of hopping conduction in doped-compensated semiconductor considers fixed impurity centres, whereas in cluster compounds strong electron-phonon interaction will change the character of correlated hopping. These issues require a deeper analysis of our results.

We have reported here the metallic and insulating phases of Nb$_4$-cluster compounds. The transport properties are dominated by electron localisation and long-range Coulomb interactions among the carriers. The metallic phase shows a minimum in resistivity. On the other hand, the insulating phase exhibits hopping conduction with $\ln \rho \sim T^{-1/2}$ dependence, suggesting the presence of a Coulomb gap at the Fermi level. These Nb$_4$ compounds show enhanced Pauli paramagnetism
and their $\chi(T)$ behaviour, including a transition at about 30 K, is similar for the insulating as well as metallic phases. Significantly, the absence of a corresponding anomaly in the transport behaviour suggests that in these compounds the transport properties are unaffected by spin degrees of freedom.

Acknowledgements: We thank Prof. Deepak Kumar for his comments and suggestions. The magnetic measurements were performed during AN’s postdoctoral Visiting Fellowship at TIFR, Mumbai.

[1] J.M. Vandenberg and B.T. Mathias, Science, 198, 194 (1977).
[2] Superconductivity in Ternary Compounds, I and II, ed. O Fischer and M.B. Maple, Topics in current Physics, 32 and 34, Springer Verlag (1982).
[3] Y. Sahoo and A.K. Rastogi, J. Phys.: Condens. Matter, 5, 5953 (1993).
[4] Y. Sahoo and A.K. Rastogi, Physica B, 215, 233 (1995).
[5] A.K. Rastogi and A. Niazi, Physica B, 223 & 224, 588 (1995).
[6] A.K. Rastogi, A. Berton, J. Chaussy, R. Tournier, M. Potel, R. Chevrel and M. Sergent, J. Low temp Phys., 52, 532 (1983).
[7] H. Ben Yaich, J.C. Jegaden, M. Potel, M. Sergent, A.K. Rastogi and R. Tournier, J. Less Common Metals, 102, 9 (1984).
[8] N. Santhi and D.D. Sarma, J. Solid State Chem., 148, 143 (1998).
[9] A. Niazi and A.K. Rastogi, J. Phys.: Condens. Matter, 13, 6787 (2001).
[10] F. Hulliger, Struct. and Bonding, 4, 83 (1968).
[11] M.A. Ruman and A.K. Rastogi, submitted to J. Phys. Chem. Solids.
[12] N.F. Mott, Metal-Insulator Transitions, 2 ed., Taylor and Francis (1990).
[13] B.I. Shklovskii and A.L. Efros, Electronic Properties of Doped Semiconductors, Springer Series in Solid State Science 45, Springer Verlag (1984).
[14] M.J. Burns and P.M. Chaikin, J. Phys. C; Solid State Phys., 18, L743 (1985).
[15] B.I. Altshuler and A.G. Aronov, Electron Electron Interactions in Disordered Systems, ed. A.L. Efros and M. Pollak (Amsterdam:Elsevier Science), 1 (1985).
[16] V.F. Shamrai and G.M. Leitus, Sov Phys. Solid State, 29, 1312 (1987).
[17] A.K. Rastogi, Current Trends in the Physics of Materials, ed. M. Youssouf, World Scientific, Singapore, 316 (1987).
[18] S. Lamba, A.K. Rastogi and D. Kumar, Phys Rev. B, 56, 3251 (1997).
[19] R.M. Hill, Phys. Stat. Sol.(a), 35, K29 (1976).
FIG. 2. (a) Resistivity and (b) thermopower versus temperature in the LT and HT phase of metallic Ga_{1.33}Nb_{4}S_{8}. (a) The HT phase shows a maximum in $\rho(T)$ around room temperature and a prominent minimum $\sim 56$ K. In comparison, the LT phase shows a monotonic increase in $\rho(T)$ above a shallow minimum $\sim 40$ K. (b) The $S(T)$ above 100 K also shows contrasting behaviour in the two phases.

FIG. 3. Temperature variation of resistivity and thermopower in insulating Ga_{1.33}Nb_{4}Se_{8}. (a) $\ln(\rho)$ versus $(1/T)$, shows non-Arrhenius behaviour over the whole $T$ range; (b) $S/(k_B/e)$ versus $(1/T)$, is temperature independent below 150 K. In the inset, $\ln(\rho)$ versus $(1/T)^{1/2}$ is linear below 150 K.

FIG. 4. Magnetic susceptibility of metallic Ga_{1.33}Nb_{4}S_{8} (S) and insulating Ga_{1.33}Nb_{4}Se_{8} (Se) plotted along with that of insulating GaNb_{4}S_{8} (S') and GaNb_{4}Se_{8} (Se') phases (ref. [7]). The metallic as well as insulating phases show similar behaviour at and below the transition around 30 K.

FIG. 5. The local moment contribution of metallic Ga_{1.33}Nb_{4}S_{8} and insulating Ga_{1.33}Nb_{4}Se_{8}. It closely follows the Langevin function (spin 1/2) which is shown by the solid curve. The inset shows the magnetisation at 2 K up till a field of 120 kOe from which the above data is extracted.
FIG. 6. Temperature variation of $\chi$ in metallic Ga$_{1.33}$Nb$_4$S$_8$ and insulating Ga$_{1.33}$Nb$_4$Se$_8$, obtained by subtracting the Curie contribution from the data of Fig. 4. The further downward trend below 6 K in our post-subtraction data could be an artifact of $\chi$ measurement at a high field of 20 kOe.