ELECTRONIC CONDUCTIVITY AND THERMOPOWER OF 
Ca$_2$NaMg$_2$V$_3$O$_{12-x}$ GARNET

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Abstract—Results are reported from conductivity and thermoelectric power measurements on partially reduced Ca$_2$NaMg$_2$V$_3$O$_{12-x}$, with $x < 5 \times 10^{-2}$, at temperatures of 300–1100 K. The conductivity is thermally activated with activation energies $0.26 \leq E_a \leq 1.28$ eV for differently reduced samples. The thermopower is temperature independent in the 300–800 K region. These results are shown to be consistent with the adiabatic hopping of small polarons localised on the vanadium sublattice, where defect interactions result in the formation of multiple conduction pathways.

1. INTRODUCTION

The garnets are compounds with general formula \{C\}_3[A\_2][D\_3]O$_{12}$ that crystallize in the cubic system with space group $O^{10}$. Here \{C\} denotes ions on dodecahedral sites, [A\_] ions on octahedral sites and (D) ions on tetrahedral sites. The three cation sublattices may accommodate a variety of ions like C = rare-earth ions, Y, Ca, Na, Sr, Pb; A = Fe, Al, Mg, Ni, Ga; D = Fe, Al, Si, Ge, V. Especially the ferrimagnetic ion garnets, such as \{Y\}_3[Fe$_2$]Fe$_3$O$_{12}$, have been widely studied [1]. Also, in the latter compound interesting light-induced changes of physical properties have been observed, and are due to the occurrence of a small amount of Fe$^{3+}$ ions on the octahedral sublattices [2]. An understanding of the charge transport mechanism is considered helpful in elucidating the physical origin of these changes. However, the presence of transition metal ions in two or three sublattices forms an extra complication, especially for the interpretation of the (photo-)conductivity results [3, 4]. Therefore, we have started a study of garnets, in which transition metal ions are only found in one sublattice.

In this article the results from a study of the charge transport mechanism in \{Ca$_2$Na\}[Mg$_2$][V$_3$]O$_{12-x}$ by means of conductivity and thermoelectric power measurements are reported. The introduction of a number of reduced vanadium ions in Ca$_2$Na-Mg$_2$V$_3$O$_{12-x}$, analogous to the Fe$^{3+}$ centres in YIG, and the occurrence of a light-induced change in the V$^{4+}$ ESR signal have been described in previous articles [5, 6].

2. THEORY

2.1 Polaronic conduction

The localisation of charge carriers may be of quite different physical origin: viz. the absence of long-range order, electronic correlations or strong electron–phonon coupling [7–10]. The mechanism of charge-carrier localisation through electron–phonon coupling, usually termed polaron formation, has been frequently adopted to describe the transport properties of transition metal oxides.

Bosman and van Daal have reviewed the results of numerous studies and summarized the conditions that determine the applicability regions of the derived expressions [11].

Briefly, a polaron consists of a charge carrier and its associated lattice distortion. On the basis of the extension of the lattice distortion, one distinguishes between large and small polarons. The large-polaron case, in which the carrier mobility is not thermally activated, is not considered here.

If the lattice distortion is confined to distances on the order of the lattice constant, the polaron is called small. Depending on the value of the electron transfer integral ($J$) with respect to the phonon energy ($h\nu_0$), two cases are considered. If $J \geq h\nu_0$, the so-called adiabatic case, an electron can tunnel several times between potential wells on adjacent atoms during an excited lattice state. At high temperatures $T > \frac{1}{4}\theta$, where $\theta$ is the characteristic temperature ($h\nu_0 = k\theta$), an approximate formula for the mobility reads

\[
\mu = (1 - c) \frac{ea^2}{kT} \nu_0 \exp\left(\frac{-E}{kT}\right),
\]

where $c$ is the fraction of occupied sites, $a$ the interstice distance, $E$ the hopping energy and the other symbols have their usual meaning. If $J < h\nu_0$, the nonadiabatic case, the mobility is of the form

\[
\mu = (1 - c) \frac{ea^2}{h} \frac{J^2}{E^{1/2}(kT)^{3/2}} \exp\left(\frac{-E}{kT}\right),
\]

with $[J^2/(hE(kT)^{3/2})] \ll \nu_0$.

According to Austin and Mott [12], an upper limit for the magnitude of $E$ in eqns (1) and (2) can be estimated using
\[ E = \frac{1}{2} E_p = \frac{e^2}{16\pi\epsilon_0\epsilon r} \text{ where } \frac{1}{\epsilon} = \frac{1}{\epsilon_s} - \frac{1}{\epsilon_0}. \quad (3) \]

\( E_p \) is the polaron binding energy, \( r \) the radius of the distorted region, \( \epsilon \) and \( \epsilon_s \) the relative static and high-frequency dielectric constants, respectively, and \( \epsilon_0 \) the dielectric constant of vacuum. Setting \( \epsilon_s \approx 5, \epsilon \approx 20 \) and \( r \approx 0.2 \text{ nm} \), a value of \( \approx 0.2 \text{ eV} \) is obtained.

2.2 Thermoelectric power in electronically conducting solids

Since the treatment of Onsager, it has been firmly established that the Seebeck coefficient, defined as the open-circuit voltage \( \Delta V \) developed across a material in a temperature gradient divided by the temperature difference \( \Delta T \) in the limit \( \Delta T \rightarrow 0 \), can be expressed as [13]

\[ \alpha = -\frac{\Delta V}{\Delta T} = \frac{S^*}{e} = - \frac{1}{e} \left( \frac{S + Q^*}{y} \right). \quad (4) \]

where \( S^* (= J_1/J_2) \), the ratio between the entropy flux \( (J_1) \) and the particle flux \( (J_2) \), is called the transported entropy. \( S \) is the particle entropy and \( Q^* \) is the heat transferred by the particle.

If electrical transport occurs via thermally activated hopping of a fixed number of localised charge carriers, the entropy term is largely determined by the entropy of mixing:

\[ S_{\text{mix}} = k \ln \left( \frac{1-c}{c} \right). \]

where \( c \) is the fraction of occupied transport sites. There is considerable evidence from both practical and theoretical studies that the heat of transfer is negligible [11, 12, 14]. The thermopower is temperature independent:

\[ \alpha = -\frac{k}{e} \ln \left( \frac{1-c}{c} \right). \quad (5) \]

According to this relation, \( \alpha < 0 \) for \( 0 < c < \frac{1}{2} \) and \( \alpha > 0 \) for \( \frac{1}{2} < c < 1 \), where \( c \) is defined as \( c = n/N \) and \( n, N \) are the concentrations of carriers and available sites. With \( N = N_0, \) the total concentration of transition metal ions concerned, eqn (5) is known as the "Heikes formula" [15]. In recent literature it has been argued that eqn (5) should be adapted to account for the electron spin degeneracy [16]. Since every empty site, i.e. a \( V^{3+} \) ion with no net spin moment (cf. also Ref. [17]), can be occupied in two ways, the entropy of mixing is

\[ S_{\text{mix}} = k \ln \frac{2^n(N-n)!}{n!} = k \ln \frac{2(1-c)}{c}. \quad (6) \]

Thus,

\[ \alpha = -\frac{k}{e} \ln \left[ \frac{2(1-c)}{c} \right]. \]

It is important to note that in both \( n \)- and \( p \)-type materials electrical transport occurs by the hopping of the same electrons over the same lattice sites. Consequently, interaction effects are to be expected at higher concentrations. This is to be contrasted with band-type conduction, where electron and hole transport take place at different energy levels in independent bands and their contributions to the thermopower can be added, weighted by the transport numbers:

\[ \left( t_i = \frac{\sigma_i}{\sigma_{\text{total}}} \right) \alpha_{\text{total}} = \alpha_e + \alpha_h. \quad (7) \]

2.3 Polarons and disorder

In the extrinsic regime, conductivity is controlled by impurities, deliberately introduced dopants or native defects. These lattice defects and foreign atoms often possess a net charge with respect to the lattice and, since they do not normally build a superstructure, destroy the periodic potential. Apart from compositional disorder, so-called positional disorder may exist in the vanadium garnet, where different atoms are simultaneously present on one sublattice [18]. Although the combined effects of disorder and electron-phonon coupling are difficult to treat theoretically, one should expect that electrons which are already localized through disorder will interact with phonons and form small polarons. Vice versa, small polarons will be situated preferably at local potential minima created by defects eq. disorder. Thus the activation energy observed in a conductivity experiment consists of two parts: a part due to electron-phonon coupling (cf. Section 2.1) and a part due to the electrostatic polaron-defect interactions. The electrostatic contribution is expected to decrease with increasing defect concentrations, since at higher concentrations a jump away from one defect is equal to a jump towards the next. Such behaviour of the activation energy has been observed in several doped transition metal oxides, and in some cases a reasonable description of the concentration dependence was obtained, assuming a random defect distribution [11, 12, 19, 20].

Yet, calculations have clearly demonstrated the importance of defect aggregation, even at low defect concentrations. For instance, according to calculations of Catlow and Stoneham in \( \text{Mn}_{1-x}\text{O} \), a rapid change from almost 100% isolated vacancies to almost 100% so-called 62 clusters already occurs at values of \( x \) between \( 10^{-4} \) and \( 10^{-3} \) [21]. The defect structure being known, the derivation of expressions for the conductivity and the thermopower is a matter of percolation theory [22].

In the absence of detailed information with respect to the defect structure, two limiting cases will be considered, as schematically depicted in Fig. 1 (a) and (b).

Figure 1 (a) refers to the case in which the energy levels of the transition metal ion sublattice are separated into discrete groups. The width of the energy
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Free energy $E$

Fig. 1. Schematic polaron site distributions; shaded areas denote occupied levels (see text).

Charge transport probably involves all levels, and the observed activation energy is predominantly determined by jumps requiring the highest activation energy. Since no electron redistributions between the different groups occur, the entropy of mixing is temperature independent. Thus, the thermopower is temperature independent, and the number of available polaron sites (cf. Section 2.2) is smaller than $N_0$, the total concentration of transition metal ions.

Figure 1 (b) represents the case in which a continuous distribution of polaron sites, wide with respect to $kT$, exists. If conduction takes place by jumps between states close to the Fermi level, the thermopower can be evaluated using the "metallic" formula [23]:

$$\alpha = -\frac{\pi^2 k^2 T}{3} \left\{ \frac{\delta \ln \sigma(E)}{\delta E} \right\}_{E=E_F}.$$

With $\sigma(E) = \sigma_0(E) \exp(-E_a/kT)$, this expression can be written as

$$\alpha = -\frac{\pi^2 k^2 T}{3} \left[ kT \left( \frac{\delta \ln \sigma_0(E)}{\delta E} \right)_{E=E_F} - \left( \frac{\delta E_a}{\delta E} \right)_{E=E_F} \right]. \quad (8)$$

Although the differentials in eqn (8) are difficult to evaluate in specific cases, a temperature-independent thermopower is not to be expected.

3. PREPARATION OF PARTIALLY REDUCED SAMPLES

Apart from the infrared spectra, which were measured on powders, all the results reported in Section 5 were obtained on two of the largest single crystals grown from PbO and V$_2$O$_5$ fluxes, with dimensions of $\sim 4 \times 4 \times 5$ and $4 \times 4 \times 3$ mm$^3$, respectively. The preparation and characterization of powder and single crystals have already been discussed in Ref. [5]. The actual composition of the single crystals is [Ca$_{2.03}$Na$_{0.69}$Mg$_{0.11}$O$_{0.34}$][Mg$_2$(V$_{2.99}$)O$_{12}$ (V$_2$O$_5$ flux) and [Ca$_{1.92}$Na$_{0.97}$Pb$_{0.10}$O$_{0.03}$][Mg$_6$V$_{27}$O$_{12}$(V$_2$O$_5$)O$_{12}$ (PbO flux), where [] denotes a cation vacancy. In the as-grown crystals no V$^{4+}$ centres could be detected by means of electron spin resonance (ESR) spectrometry [5]. Therefore, the crystals were subjected to a reduction treatment at elevated temperatures in air or CO/CO$_2$ gas mixtures and subsequently quenched to room temperature (cf. Table 1).

The crystals were first heated for $\sim 15$ min at 1130°C in air, this was followed by an air quench to room temperature (fast quench). However, previously reported photosensitivity experiments indicated a marked influence of the thermal history of the crystals on the observed physical properties [6]. Therefore, it was attempted to standardize the pretreatment conditions by performing the reduction reaction in the

Table 1. Pretreatment conditions of the garnet crystals

<table>
<thead>
<tr>
<th>sample number</th>
<th>flux composition</th>
<th>quenching rate</th>
<th>temperature (°C)</th>
<th>log $P_{O_2}$ (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca$<em>2$NaMg$</em>{2}$V$<em>3$O$</em>{12}$</td>
<td>as grown</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>fast + partially oxidised at 700°C</td>
<td>1130</td>
<td>+4.3</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>medium</td>
<td>760</td>
<td>-11.3</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>medium</td>
<td>760</td>
<td>-10.5</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>slow</td>
<td>775</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>fast</td>
<td>1120</td>
<td>+4.3</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>slow</td>
<td>775</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>medium</td>
<td>760</td>
<td>14.7</td>
</tr>
<tr>
<td>9</td>
<td>Ca$<em>2$NaMg$</em>{2}$V$<em>3$O$</em>{12}$</td>
<td>as grown</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>fast</td>
<td>1130</td>
<td>+4.3</td>
</tr>
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</table>
conductivity cell in a CO/CO₂ atmosphere. The relatively large thermal mass in that case imposes slow quenching rates, and, to avoid carbon deposition, the CO/CO₂ mixture had to be replaced by purified argon before quenching. Finally, some reduction experiments were performed in a Setaram-type MTB 10-8 microbalance (medium quenching rate). Although incoherent results for remounted samples cast some doubt on the correspondence between the apparent weight loss and the oxygen deficiency, an upper limit of x ~ 5 × 10⁻² in Ca₂NaMg₂V₃O₁₂₋ₓ can be estimated from the maximum stable weight losses recorded.

4. EXPERIMENTAL DETAILS

The quenched single crystals were spring-mounted between platinum electrodes in an alumina sample holder with an empty cell resistance of ~10¹¹ Ω at room temperature. Good electrical contact was achieved by platinum painting the contact areas (Leitplatin 308A Demetron). Most of the conductivity measurements were performed with a Keithley 616 Digital Electrometer operating in the resistance mode. Occasionally, the systems were checked for frequency dispersion in the range 0.05–10⁴ Hz with a Solartron Frequency Response Analyser 1174. The sample holder was furnished with two platinum wire resistance heating elements, which could be independently controlled, to supply the temperature gradient for the thermopower measurements. By using two heating blocks, the average temperature is easily kept constant within ±1°C, while at the same time the ΔT range is effectively doubled without increase of ΔTmax because the temperatures can be inverted. The thermal response of the system is such that a few minutes after a change of settings the thermocouple readings have stabilised within 1 µV. To ensure good correspondence, thermopower and conductivity measurements were performed directly one after the other. The Seebeck coefficients were calculated by a least squares analysis from plots of ΔV vs ΔT consisting of eight data points, and the maximum temperature difference employed was limited to ~10°C. These plots were linear and, with a variance of ±1°C, always went through the origin, apart from exceptions at high temperatures, which are explicitly discussed in the following section. At low temperatures the measurement range is limited by the sample resistance. At resistance values higher than ~5 × 10⁶ Ω electrical noise caused by the heating coils and spurious voltages inevitably present leads to erratic results. The reported Seebeck coefficients are not affected by the heating currents, since operating the system at the same average temperature but 30°C, respectively, 150°C, above the temperature of the main furnace resulted in identical thermopower values.

To prevent reoxidation of the samples, the cell was continuously purged with purified argon, and the measurements were performed with increasing temperature, contrary to common practice. Infrared lattice spectra were recorded in the 100–1000-cm⁻¹ region using a Bruker Infrared Fouriertransform Spectrometer IFS. For the 100–700-cm⁻¹ region the finely divided powder samples were embedded in polyethylene; for the 400–1000-cm⁻¹ region the samples were embedded in KBr pressed pellets.

5. RESULTS AND DISCUSSION

The samples exhibited linear current–voltage characteristics for 10⁻³–10 V, and no frequency dispersion of the conductivity was observed in the 0.05–10⁴-Hz region. Therefore, the experimental data are assumed to correspond to electronic bulk conductivities. In Figs. 2 and 3 the measured conductivities (σ) of several partially reduced Ca₂NaMg₂V₃O₁₂₋ₓ single crystals are plotted as log σ vs reciprocal temperature. These results are representative of a larger body of experimental data. Generally, reproducible values were recorded on thermal cycling up to 700 K. Heating to higher temperatures, however, resulted in
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The data were corrected for the thermopower of the platinum measurement leads [24]. Inspection of the figures shows that the Seebeck coefficients of most of the samples are temperature independent up to $\sim$800 K. This is a strong indication of a constant number of charge carriers; thus, the thermally activated conductivity is due to a thermally activated mobility of the charge carriers. Unfortunately, the concentration of the carriers ($N_c$) in the individual samples cannot be evaluated from the Seebeck coefficients alone, since the concentration of available polaron sites ($N$) is not known. Nevertheless, from a comparison of the observed conductivities with the pretreatment conditions (cf. Table 1), it can be concluded that, generally, an increased oxygen deficiency results in higher conductivities and lower activation energies. The magnitudes of the observed activation energies clearly exceed the limiting value derived, assuming localization due to electron–phonon coupling only, and indicate considerable electrostatic contributions [cf. eqn (3) and Section 2.3].

Next we shall attempt to calculate $N$ from the preexponential factors given in Table 2.

The fraction of occupied transport sites ($c$) can be evaluated from the Seebeck coefficients via eqn (6). To obtain an estimate of the optical phonon frequency ($\nu_0$), infrared lattice spectra were recorded (cf. Fig. 6). Characteristic features of these spectra are a set of bands in the 800–600 cm$^{-1}$ region and a strong band in the region around 400 cm$^{-1}$. Similar spectra are known for aluminium, iron and germanium garnets [17, 25].

Raman spectra of Ca$_2$NaMg$_2$V$_2$O$_{12.2}$, reported by White et al. [26], also show a series of peaks in the same spectral region. A peak around 850 cm$^{-1}$ is assigned to a tetrahedral vibrational mode. Although

![Figure 3. Conductivity–temperature product vs reciprocal temperature of Ca$_2$NaMg$_2$V$_2$O$_{12.2}$ single crystals grown from a V$_2$O$_5$ flux; numbers correspond to pretreatment conditions given in Table 1.](image)

Table 2. Activation energy and preexponential coefficient obtained by fitting conductivity data for Ca$_2$NaMg$_2$V$_2$O$_{12.2}$ samples to eqn (9)

<table>
<thead>
<tr>
<th>curve number</th>
<th>$E_a$ (eV)</th>
<th>$\log N_c(1-c)\nu_0^2a^2/L/k$ (G$^{-1}$ m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.19</td>
<td>6.24</td>
</tr>
<tr>
<td>2</td>
<td>1.24</td>
<td>7.25</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>4.34</td>
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<tr>
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<td>0.77</td>
<td>4.71</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>4.84</td>
</tr>
<tr>
<td>6</td>
<td>0.70</td>
<td>5.96</td>
</tr>
<tr>
<td>7</td>
<td>0.58</td>
<td>2.90</td>
</tr>
<tr>
<td>8</td>
<td>0.26</td>
<td>2.56</td>
</tr>
<tr>
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<td>1.28</td>
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</tr>
<tr>
<td>10</td>
<td>1.10</td>
<td>7.35</td>
</tr>
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</table>
there is no unambiguous assignment of the different vibrational modes, a value of \( v_0 \sim 3 \times 10^{13} \text{ s}^{-1} \) seems a reasonable estimate.

The concentrations of available polaron sites calculated using \( v_0 = 3 \times 10^{13} \text{ s}^{-1}, \alpha = 0.38 \text{ nm}, \) the nearest neighbour V-V distance and \( c \) values obtained via the Seebeck coefficients increase exponentially from \( N = 2 \times 10^{23} \text{ m}^{-3} \) at \( E_a = 0.26 \text{ eV} \) to \( N = 10^{24} \text{ m}^{-3} \) at \( E_a = 1.24 \text{ eV} \). However, the maximum density of available polaron sites that is physically meaningful is equal to the total vanadium ion concentration, \( 1.25 \times 10^{28} \text{ cm}^{-3} \). Evidently, an optical phonon frequency of \( \sim 10^{16} \text{ s}^{-1} \) is impossible. Therefore, it is concluded that in these vanadium garnets, where coulombic defect interactions dominate the charge transport behaviour, illustrated by the large variation in activation energies, \( 0.26 < E_a < 1.28 \text{ eV} \), the correct fraction of occupied transport sites is not obtained via eqn (6). In this respect it is instructive to consider the distribution of polaron sites schematically depicted in Fig. 1(a). If the density of polaron sites belonging to the partially filled group is too low to construct continuous conduction pathways through the crystal, charge transport will necessarily involve electron jumps over sites belonging to the other groups. In such case the conductivity will be predom-
inantly determined by jumps requiring the highest activation energies. However, unlike the situation in which parallel transport processes are occurring [cf. eqn (7)], the Seebeck coefficient for a series circuit is a summation over individual terms $\alpha = \sum_{\text{groups}} \alpha_i$. Since this equation does not contain the transport numbers, an effective fraction of occupied transport sites is not obtained via eqn (6). Also, it is noted that the product $E_c(1 - c)$ decreases with increasing reduction degree of the samples (cf. Tables 1 and 2). Apparently, whilst the total amount of $V^{4+}$ is increasing, the effective carrier concentration $N_c$ that determines the conductivity is decreasing. In the schematic representation of Fig. 1 (a) the effective carriers are situated on polaron sites requiring the highest activation energies in regions where the local $V^{4+}$ concentration is low. As mentioned before, the interaction between defects increases with increasing $V^{4+}$ concentration. Therefore, we have to conclude that the number of jumps requiring high energies decreases accordingly. Thus, in the case of charge transport by small polaron hopping between inequivalent sites, detailed information regarding the actual defect structures is required to correlate the fractions $c$ in eqn (6) with $c$ in eqn (9) and the concentrations $N_c$ in eqn (9) with $[V^{4+}]_{\text{loss}}$. Further, it is not possible to separate the effects of defect interactions at a fixed reduction degree and a possibly inhomogeneous sample reduction inherent in the quenching procedures (Section 3). Evidence for the occurrence of such an inhomogeneous distribution can be inferred from the alternating sequence of, for example, curves 3–5 in the $\alpha$ and $\sigma$ plots (Figs. 2 and 3).

Nevertheless, if the energy difference between the groups is large enough to prevent a redistribution of electrons over the groups at the temperatures of measurement, the observed thermopower is temperature independent. Thus, the above results ascertain that charge transport occurs by means of thermally activated hopping of electrons via the vanadium sublattice, where defect interactions determine the number of different conduction paths and activation energies. Deviations between the experimental Seebeck coefficients and those calculated via eqn (6), in cases where the deviation from stoichiometry or the dopant concentrations were known, have been reported repeatedly and are usually attributed to a complex defect structure [14, 22, 27, 28]. The occurrence of different $V^{4+}$ centres in the vanadate garnet, even at low defect concentrations is further substantiated by ESR experiments [6].

Using

$$\mu = \frac{(1 - c) \rho_{\text{electronic}}}{k T} \exp \left( -\frac{E_h}{k T} \right)$$

with $(1 - c) \approx 1$, $a = 0.48$ nm and $\rho_{\text{electronic}} = 3 \times 10^{15}$ s$^{-1}$, mobility estimates of $\mu \approx 3 \times 10^{-7}$ m$^2$/Vs and $\mu \approx 10^{-14}$ m$^2$/Vs for $E_h = 0.25$ and 1.0 eV, respectively, are obtained at $T = 500$ K.

With respect to the intervanadium distance, it is noted that, considering the charge transport mechanism of a series of doped vanadium spinels, Goodenough observed a transition from itinerant to localized electron behaviour at an intervanadium distance of $\approx 0.29$ nm [27]. The shortest intervanadium separation in the vanadate garnet is much larger, 0.38 nm, favouring a localised behaviour. The number of other garnet materials where the charge transport mechanism has been established is limited and mainly concerns doped and undoped yttrium iron garnet. For this compound the majority of experimental results favour the applicability of the large polaron model at high temperatures, $T > 600$ K, and the small polaron model at low temperatures, $T < 300$ K [3]. On the other hand, in gadolinium and dysprosium iron garnet the charge transport at elevated temperatures, $T > 600$ K, has been ascribed to thermally activated hopping of holes via the iron lattice sites [29, 30]. In $\{\text{Ca},_{\text{1-x}},\text{Y},_{\text{x}}\}\{\text{Mn}_2\}\{\text{Ge}_2\}\text{O}_{12}$ the charge transport is also attributed to thermally activated hopping of small polarons localized on the manganese sublattice, where defect interactions limit the number of available transport sites [17].

The arrows on the curves in Fig. 4, denoting the onset of a rapid change in the measured Seebeck coefficients with increasing temperature, have not been discussed so far. The voltages obtained correspond to physically unrealistic charge-carrier concentrations, whereas in the same temperature region no abrupt changes in the conductivity were observed. However, in this temperature region a displacement of the linear $\Delta V$ vs $\Delta T$ plots away from the origin (cf. Section 4) was observed, indicating the appearance of additional voltages. The occurrence of an increased reoxidation rate at the same time is probably due to an increased ionic mobility. Therefore, the additional voltages are attributed to rearranging defects. If these voltages and the electronic thermovoltages become comparable in magnitude, erratic $\sigma$ values are to be expected. Similar effects are thought to be responsible for the curvatures of lines 3 and 7, whereas the deviation of line 8 is due to reoxidation of the sample, as was demonstrated by a decrease in conductivity (cf. Fig. 4). Similar changes in the recorded thermopower values at high temperatures, due to compositional relaxation in the temperature gradient, have been observed in $\text{Ca}_{x-\gamma}\text{Y},_{\gamma}\text{Mn}_2\text{Ge}_2\text{O}_{12}$ [17].

Finally it is noted that the differences in composition and impurity content between the crystals grown from PbO and $V_2O_5$ fluxes apparently do not affect the conductivity properties, as demonstrated by the similarity of curves 1 and 9 (cf. Figs. 2 and 3). Thus, in the untreated crystals also, the conductivity is probably determined by the oxygen deficiency.

6. SUMMARY AND CONCLUSIONS

The thermopower of partially reduced $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12.5}$ is temperature independent in the region 300–800 K. The conductivity is thermally activated, while large differences in activation energy
0.26–1.28 eV are observed with varying $V^{4+}$ content. The magnitudes of the measured Seebeck coefficients, for differently pretreated samples, indicate a complex defect structure. Therefore, the charge transport in Ca$_2$NaMgV$_x$O$_{2.5-x}$ is attributed to thermally activated hopping of small polarons via the vanadium sublattice, where defect interactions determine the number of different conduction paths and activation energies.

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