Band-width control in a perovskite-type 3d^1 correlated metal Ca_{1-x}Sr_xVO_3. I. Evolution of the electronic properties and effective mass.

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Single crystals of the perovskite-type 3d^1 metallic alloy system Ca_{1-x}Sr_xVO_3 were synthesized in order to investigate metallic properties near the Mott transition. The substitution of a Ca^{2+} ion for a Sr^{2+} ion reduces the band width W due to a buckling of the V-O-V bond angle from ∼180° for SrVO_3 to ∼160° for CaVO_3. Thus, the value of W can be systematically controlled without changing the number of electrons making Ca_{1-x}Sr_xVO_3: one of the most ideal systems for studying band-width effects. The Sommerfeld-Wilson’s ratio (∼2), the Kadowaki-Woods ratio (in the same region as heavy Fermion systems), and a large T^2 term in the electric resistivity, even at 300 K, substantiate a large electron correlation in this system, though the effective mass, obtained by thermodynamic and magnetic measurements, shows only a systematic but moderate increase in going from SrVO_3 to CaVO_3, in contrast to the critical enhancement expected from the Brinkmann-Rice picture. It is proposed that the metallic properties observed in this system near the Mott transition can be explained by considering the effect of a non-local electron correlation.

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I. INTRODUCTION

Despite extensive investigations on 3d transition-metal (TM) oxides, there remain many more mysteries still to unravel. The discoveries of metal-to-insulator transitions (MIT) in 3d TM oxides with a partially filled 3d band, for example, has given us great incentive to re-examine several previous studies of the electronic states in these TM oxides.

The most important feature of this kind of 3d TM oxides is that simple one-electron band theory is no longer sufficient to give a good account of the electronic states, since the electron correlations are much larger than expected for the one-electron band-width. Mott first introduced the concept of MIT caused by a strong Coulomb repulsion of electrons. Although the description of the MIT (Mott transition) is still argued from various points of view, a more challenging problem lies in the metallic phase near the Mott transition, where a narrow-band system is known to show anomalous metallic properties, and substantial enhancement of the fluctuations of spin, charge and orbital correlations is observed. This problem has been investigated with renewed vigor since the discovery of high-T_c cuprate superconductors and although a number of enlightening works have been done so far, still we cannot grasp a comprehensive view of the whole physics.

As one of the open questions, in this paper, we focus on the problem of the effective mass in the perovskite-type 3d^1 correlated metal Ca_{1-x}Sr_xVO_3. An important manifestation of the mass enhancement in the perovskite-type light-3d TM oxides has been given by Tokura et al. They reported filling-dependent electronic properties in the Sr_{1-x}La_xTiO_3 system near the MI transition around x = 1. The LaTiO_3 (x = 1) material behaves as an insulator below 300 K and antiferromagnetic ordering of Ti S = 1/2 spins occurs at T_N = 120 ∼ 150 K. They also reported that Fermi-liquid-like behavior was observed even in the immediate vicinity of the MI phase.
boundary, with a critical increase of $m^*$ arising from the effect of the enhanced electron correlations. Within the framework of Fermi-liquid theory, the only way to approach MIT continuously is to realize the divergence of the single-quasi-particle mass $m^*$ at the MIT point. The critical behaviors observed in the Sr$_{1-x}$La$_x$TiO$_3$ system are fairly systematic, thus provoking intense theoretical study; however there is still room for arguments, especially in the following points:

1. Tokura et al. compared the effective mass $m^*$ to the free electron mass $m_0$. However, the $x$-dependence of the “band-mass” $m_b$ should also be taken into account. Compared with the value of $m_b$ for the similar system CaVO$_3$, the mass enhancement of the Sr$_{1-x}$La$_x$TiO$_3$ system is not so large, except for the region $x > 0.95$.

2. The critical increase of the value of $m^*$ in the Sr$_{1-x}$La$_x$TiO$_3$ system is only seen in the region very close to MI transition boundary. However, in this region, it is not obvious whether Fermi-liquid theory is still valid. In fact, in the region of significant mass-enhancement ($x > 0.95$), the number of carriers seems to be depleted.

3. Another filling-dependent MI transition is observed in the Y$_{1-x}$Ca$_x$TiO$_3$ system. However MIT occurs around $x = 0.4$ which is relatively far from integral filling. Nevertheless, the effective mass shows a conspicuous enhancement in the vicinity of MIT similar to that seen in the Sr$_{1-x}$La$_x$TiO$_3$ system. Thus, it seems reasonable to suppose that this kind of mass-enhancement, observed in those “filling-control” systems close to MIT, might be induced by fluctuations or inhomogeneity of the insulating phase near the boundary of MIT.

The above problems can be due to the fact that the critical behaviors depend on a path along which a system approaches the boundary of MIT. In the Sr$_{1-x}$La$_x$TiO$_3$ system, the band-filling is dominantly controlled instead of the band-width.

The question then arises; how does the effective mass in the metallic state actually change as we change solely the electron correlation without changing the band-filling? In order to elucidate this issue, another type of systematic experiment is required; i.e., we need to control only the 3$d$ band width $W$ in a particular system while keeping the number of carriers fixed.

Representative examples are the pressure-induced MIT reported in V$_2$O$_3$, where hydrostatic pressure modifies $W$. However, for a quantitative discussion, we need to know the change of the lattice constants under pressure. Moreover, in general, the anisotropic compressibility due to the anisotropy of the lattice structure affects $W$ in a complex manner. Other examples are found in nickel-based compounds: the perovskite-type RNiO$_3$ with $R$ of the trivalent rare-earth ions (La to Lu), and the pyrite-type chalcogenide system NiS$_{2-x}$Se$_x$. The insulating state of these nickel compounds is classified as a charge-transfer insulator rather than a Mott-Hubbard insulator in the so-called Zaanen-Sawatzky-Allen classification scheme of TM compounds. Therefore, MIT occurs as a closing of the charge-transfer gap with increase of the $p$-$d$ hybridization. Thus, it is inevitable that MIT is not described by the simple model of the Mott transition and the metallic state is more complicated.

Based on these considerations, we have synthesized a solid solution of the perovskite-type metallic vanadates, CaVO$_3$ and SrVO$_3$, in order to investigate the metallic state near the Mott transition more simply with a systematic band-width control. We have succeeded in obtaining single crystals of the homogeneous metallic alloy system Ca$_{1-x}$Sr$_x$VO$_3$ with nominally one 3$d$ electron per vanadium ion. In the Ca$_{1-x}$Sr$_x$VO$_3$ system, as we isovalently substitute a Ca$^{2+}$ ion for a Sr$^{2+}$ ion, a lattice distortion occurs. This is governed by the so-called tolerance factor $f$ of the perovskite-type compounds ABO$_3$ defined as

$$f = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)},$$

where $R_A$, $R_O$, and $R_B$ are the ionic radii of the A ion, the O ion (oxygen), and the B ion, respectively. When the value of $f$ is almost 1, the system is cubic; while for $f < 1$, the lattice structure changes to rhombohedral and then to the orthorhombic GdFeO$_3$ type. In the GdFeO$_3$ structure, it is known that the B-O-B bond angle decreases continuously with decreasing $f$ almost irrespective of the set of A and B. According to the literature, the ionic radii of Ca$^{2+}$, Sr$^{2+}$, V$^{4+}$, and O$^{2-}$ ions are 1.34, 1.44, 0.58, and 1.40 Å, respectively. Thus we obtain a value of $f$ of 1.014 for SrVO$_3$, and 0.979 for CaVO$_3$, corresponding to a V-O-V bond angle of $\sim 180^\circ$ for SrVO$_3$ and $\sim 160^\circ$ for CaVO$_3$. The buckling of the V-O-V bond angle reduces the one-electron 3$d$-band width $W$, since the effective 3$d$-electron transfer interaction between the neighboring V-sites is governed by the supertransfer process via the O 2$p$ state.

Thus, the ratio of the electron correlation $U$ normalized to $W$ ($U$ is considered to be kept almost constant by the substitution) can be systematically controlled in Ca$_{1-x}$Sr$_x$VO$_3$ without varying the nominal carrier concentration. Furthermore, the V-O-V bond angle of CaVO$_3$ ($\sim 160^\circ$) is almost equal to insulating LaTiO$_3$, so it is reasonable to consider that CaVO$_3$ is close to the MIT boundary and thus is an ideal system for the investigation of the metallic state near the Mott transition. In fact, some spectroscopic manifestation of the strong electron correlation has been reported already, showing that there is significant spectral weight redistribution in the Ca$_{1-x}$Sr$_x$VO$_3$ system. Therefore, the effective mass of this system, especially at the $x = 0$ end (CaVO$_3$), is expected to be enhanced as discussed for Sr$_{1-x}$La$_x$TiO$_3$ near the insulating composition LaTiO$_3$.

Nevertheless, the Ca$_{1-x}$Sr$_x$VO$_3$ system does not show such a significant enhancement of the effective mass. The goal of this paper is to reveal intriguing behavior in the evolution of the effective mass, as we control the $U/W$
ratio in this system. Details of the experiments, especially the method of preparing single crystals of this new vanadate system, are described in Sec. III. We discuss the cubic-orthorhombic lattice distortion in Sec. III A. The results from magnetic susceptibility measurements and the obtained effective mass $m^*$ are shown in Sec. III B and compared to $m^*$ deduced from the electronic specific heat coefficient in Sec. III C. The Sommerfeld-Wilson’s ratio is found to be almost equal to 2, that is strong evidence of the large electron correlation. The electric resistivity data are analyzed by a model incorporating the electron-electron interaction ($T^2$ term) as well as the electron-phonon interaction (Bloch-Gruneisen term) in Sec. III D. It is noted that the Kadowaki-Woods ratio lies in the same region as the heavy Fermion compounds. Finally, we discuss the effect of non-local electron correlations, i.e., the momentum-dependent self-energy, which can be significant near the Mott transition. In order to explain consistently both the strong electron-correlations and the missing enhancement of the effective mass.

II. EXPERIMENTAL

A ‘ceramic method’ was employed in order to prepare poly-crystalline samples. 4N CaCO$_3$, SrCO$_3$ and VO$_2$ were used as starting reagents. We prepared CaO and dried SrCO$_3$ by pre-heating both the CaCO$_3$ and SrCO$_3$ compounds in air for 24 hours at 1000°C, and weighed the powders while they were still over 100°C. We confirmed that the dried CaO and SrCO$_3$, as well as VO$_2$, were all single phase by x-ray diffraction (XRD). The starting compounds, CaO, SrCO$_3$, and VO$_2$ were then mixed in the required molar ratio Ca : Sr : V = $1 - x : x : 1$ and then calcined several times at 1250°C in flowing argon atmosphere for 24 hours. We found that the reaction proceeds in the solid state, the reaction rate depends on the diffusion rate of the constituents through the product phases. As the reaction proceeds, diffusion paths become longer, and hence the reaction rate decreases. Therefore the intermittent mechanical grinding of the reaction product is important in this method.

As the Sr concentration is increased, it is required to add hydrogen-gas at a rate up to about 50 cc/min. The amount of hydrogen-gas flow for each calcination process must be controlled in order to avoid too much reduction and peroxidization. The amount of the oxidation was conveniently checked by examining the XRD spectrum, i.e. the lattice constants, of the reaction product every time after the intermittent grinding. This process was repeated until completion of the reaction.

Finally, the powder was put into rubber tubes and each tube was pressed under hydrostatic pressure of 1000 atm to form a cylindrical rod of 6 mm diameter and 10 cm length. The rods were sintered at 1300°C in the same atmosphere described above.

Single crystals of Ca$_{1-x}$Sr$_x$VO$_3$ were grown by the floating zone (FZ) method in an infrared-radiation furnace (Type SC-N35HD, Nichiden Machinery Ltd.) with two 1.5kW halogen lamps as radiation sources. At first, the sintered rod is cut into two parts: one is 2 cm long for the “seed” rod, which is held at the top of the lower-shaft, and the rest of the sintered rod, called the “feed” rod, is suspended at the bottom of the upper-shaft. Each rod is rotated at about 20 rpm in opposite directions. The lamp power is raised gradually until both the rods are melted, then the molten zone is attached to the top of the seed. The molten zone is passed through the whole feed rod at a rate of about 1 cm/hour in flowing argon atmosphere without any interruption or change of lamp power. The most important point here is to control the reduction atmosphere delicately, depending on the amount of the Sr content x, and also on the oxygen stoichiometry of the feed rod. As we increase the value of x, it is necessary to add less than 0.1% hydrogen to the flowing argon. As soon as this small amount of hydrogen is added, however, the melting temperature rises drastically, and the molten zone shrinks unless we increase the lamp power once more. On the other hand, if the amount of hydrogen gas is not sufficient, the liquid phase in the molten zone loses viscosity and spills by degrees along the rod. Furthermore, a different phase, which might be a peroxided phase, appears in the molten zone and precipitates on the surface of the zone to form an “antler”. Thus, a delicate feed-back control of the amount of hydrogen gas and the power of the halogen lamp is necessary to obtain a single crystal with sufficient quality. Typical dimensions of a single-crystalline grain in the resultant rods are $2 \times 1 \times 1$ mm$^3$.

Each crystal was examined by powder XRD and by Laue photography to check for homogeneity. Results are summarized in the next section.

The oxygen off-stoichiometry in Ca$_{1-x}$Sr$_x$VO$_3$ was determined using a Perkin-Elmer TGA-7 thermogravimetric (TG) analyzer from the weight gain on heating the sample to around 1300 K in flowing air and assuming that the final oxidation state of a vanadium ion was +5. Neither weight gain due to peroxidation, nor weight loss due to desorption of the oxygen was observed, once the highest-oxidized material (Ca$_{1-x}$Sr$_x$)$_2$V$_2$O$_7$ was obtained.

As-prepared samples contain a certain amount of oxygen defects. The result of the TG measurements indicated that, with increasing temperature, the samples are abruptly oxidized at around 420 K. Moreover, after this oxidation, the oxygen concentration of the samples becomes stoichiometric and no further oxidation occurs until the temperature reaches around 700 K. Therefore, we were able to prepare samples without any oxygen off-stoichiometry by annealing the samples in air at about 200°C for around 24 hours.

The stoichiometry of the ratio Ca : Sr : V = $1 - x : x : 1$ was confirmed by an inductively coupled plasma atomic emission spectrometer (SEICO, SPS7000). The amount of off-stoichiometry in the single-crystalline samples was within the error bar, i.e., less than 1%.

In order to perform the dc-electric resistivity measurement, the single crystalline samples were cut and shaped
III. RESULTS AND DISCUSSION

A. Lattice constants

The XRD patterns of Ca$_{1-x}$Sr$_x$VO$_3$ for varying Sr content are displayed in Fig. 1 and the deduced lattice parameters are shown in Fig. 2. The lattice parameters change systematically from the orthorhombic CaVO$_3$ to SrVO$_3$ which is simple-cubic within the error bar (~ ±0.2%). According to the four-axes XRD measurement, the lattice constants of CaVO$_3$ are $a = 0.53185(8)$ nm, $b = 0.7543(2)$ nm, and $c = 0.53433(8)$ nm. The V-O-V bond angle is 154.3$^\circ$ for V ions on the ac-plane (V-O bond length is 0.1891(6) nm) and 171.0$^\circ$ for V ions along the b-axis (V-O bond lengths are 0.190(0) nm and 0.196(5) nm). This large buckling of the V-O-V bond angle (~160$^\circ$ in average) is considered to make the one-electron 3d band-width $W$ of this system smaller than that of SrVO$_3$, where the V-O-V bond angle is almost exactly 180$^\circ$.

B. Magnetization

Figure 3 shows the temperature-dependence of the magnetic susceptibilities $\chi$ of Ca$_{1-x}$Sr$_x$VO$_3$ at 5 Tesla $= 50000$ Oe. Since none of the samples showed any significant hysteresis between the heating and cooling cycles, we have plotted data for the heating process only. The field-dependence of the magnetization $M$ of SrVO$_3$ is plotted in Fig. 4. We measured $M$ up to 5 Tesla while increasing and decreasing the applied field $H$ at both 5 K and 300 K. At 300 K, the magnetization curve shows no hysteresis and $M$ depends linearly on $H$. This means that only paramagnetic moments contribute to the total magnetization. When we decrease the temperature to 5 K, the magnetization curves become hysteretic and also
show a slight upturn.

During the heating and cooling cycles.

We have so far reported the effects of the (unavoidable) oxygen off-stoichiometry in CaVO$_3$ by intentionally introducing the oxygen defects in varying degrees.\textsuperscript{23,28,29} In this study, although we tried to prepare oxygen-stoichiometric samples using a delicate annealing procedure, there still exists a very small but irreducible amount of inevitable oxygen defects.

Local moments due to these oxygen defects contribute to $M$ as a spontaneous magnetization or in this case a sublattice magnetization, because the Weiss temperature is negative. The value of $M$ is very small compared with that observed in CaVO$_{2.8}$\textsuperscript{29} and is consistent with the number of local moments deduced from the Curie constants (vide infra).

All the magnetic susceptibility data $\chi$ are well reproduced by the following formula:

$$\chi_P + \chi_{\text{dia}} + \chi_{\text{core}} + \chi_{\text{orb}} + \frac{C}{T - \vartheta} + \alpha T^2,$$

where $\chi_P$ is the Pauli paramagnetic term, $\chi_{\text{dia}}$ is the Landau diamagnetization, $\chi_{\text{core}}$ comes from the diamagnetic contribution of the core-levels, and $\chi_{\text{orb}}$ is due to the orbital Van Vleck paramagnetization. The Curie-Weiss term is attributed to impurities such as the native oxygen defects. The last term is considered to originate from the higher-order temperature-dependent term in the Pauli paramagnetism, that is neglected in the zeroth order approximation, and reflects the shape of the density of states (DOS) $D(\omega)$ Ryd$^{-1}$/ formula-unit at the Fermi energy $E_F$.

The first two terms are re-written using the effective mass $m^*$ and the bare band mass $m_b$ of the system [we employ $m_b$ deduced from the band calculation using a local density approximation (LDA)]\textsuperscript{30} rather than $m_b$ of the non-interacting Bloch electrons:

$$\chi_{\text{spin}} = \chi_P + \chi_{\text{dia}} = \left(\frac{m^*}{m_b} - \frac{m_b}{3m^*}\right) \chi_P^{\text{LDA}},$$

where $\chi_P^{\text{LDA}}$ stands for the Pauli paramagnetic term deduced from the LDA band calculation:

$$\chi_P^{\text{LDA}} [\text{emu/mol} \equiv \text{erg Oe}^{-2} \text{mol}^{-1}] = N \mu_B^2 D(E_F) = 2.376 \times 10^{-6} \times D(E_F),$$

where $N \text{mol}^{-1}$ is the number of itinerant electrons per one mole of unit formula and $\mu_B = 9.274 \times 10^{-21} \text{erg Oe}^{-1}$.\textsuperscript{31}

For the third term $\chi_{\text{core}}$, we have used the values given in the literature,\textsuperscript{32} as summarized in Table I. For the fourth term, we used an $x$-independent value\textsuperscript{33} of $\chi_{\text{orb}} = 6.5 \times 10^{-5} \text{emu/mol}$ estimated in another 3$d^1$ metallic vanadate system VO$_2$.\textsuperscript{34} Hence, we can fit Eq. (1) to the observed data.

The obtained values of the Curie-Weiss term $C$ are as small as $0.5 \sim 2.2 \times 10^{-3} \text{emu K/mol}$, and the Weiss
from \( \chi \) perform the measurement up to higher temperatures. It is inevitable in ABO

...vas that only 0.22% of the V sites have the

...nt magnetism is negligible in the temperature range we mea-

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...h a temperature-independent Pauli param-

...metry is negligible in the temperature range we mea-

...ed in Fig. 5. The value of \( m^* \) is plotted against Sr content.

...antiferromagnetic interaction among the local moments.

...nteracting limit \( \gamma^{LDA} \):

\[
\gamma^{LDA} = \frac{\pi^2}{3} k_B^2 N D(E_F) ,
\]

where \( N \) is the number of itinerant electrons per mole in the

...s is to measure \( \chi^\ast \) from magnetic susceptibility data with Eq. 1 and Eq. 2, where \( \chi_{core} \) and \( \chi_{orb} \) are fixed to the values in the literature.\(^32,34\) \( \chi_P \) and \( \chi_{LDA} \) are calculated from \( D(E_F) \) obtained by the LDA band calculation.\(^30,31\)

| \( x \) | \( \chi_{spin} \) (emu/mol) | \( \chi^{LDA}_P \) (emu/mol) | \( m^*/m_b \) |
|---|---|---|---|
| 0.00 | \( 2.008 \times 10^{-4} \) | \( 6.651 \times 10^{-5} \) | 3.126 |
| 0.20 | \( 1.905 \times 10^{-4} \) | \( 6.454 \times 10^{-5} \) | 3.060 |
| 0.25 | \( 1.904 \times 10^{-4} \) | \( 6.405 \times 10^{-5} \) | 3.081 |
| 0.50 | \( 1.788 \times 10^{-4} \) | \( 6.159 \times 10^{-5} \) | 3.013 |
| 0.70 | \( 1.678 \times 10^{-4} \) | \( 5.963 \times 10^{-5} \) | 2.929 |
| 0.80 | \( 1.678 \times 10^{-4} \) | \( 5.865 \times 10^{-5} \) | 2.973 |
| 1.00 | \( 1.606 \times 10^{-4} \) | \( 5.668 \times 10^{-5} \) | 2.946 |

C. Electronic specific heat coefficient

An alternative method to evaluate \( m^* \) is to measure the electronic contribution to the specific heat, \( \gamma T \), which reflects DOS at \( E_F \). \( \gamma \) is called the electronic specific heat coefficient. Using \( D(E_F) \) \( \text{Ryd}^{-1} \) / formula-unit obtained by the LDA band calculation,\(^31\) we can deduce the value of electronic specific heat coefficient in the non-interacting limit \( \gamma^{LDA} \):

\[
\gamma^{LDA} = \frac{\pi^2}{3} k_B^2 N D(E_F) ,
\]

where \( N \) is the number of itinerant electrons per mole in the unit formula. Then,

\[
\gamma^{LDA} \text{[mJ mol}^{-1}\text{K}^{-2}] = 0.173238 \times D(E_F) .
\]

The ratio of the effective mass to the band mass (\( m^*/m_b \)) is deduced from the ratio of the observed \( \gamma \) to the calculated \( \gamma^{LDA} \).

Sufficiently below the Debye temperature \( \Theta \), the constant volume specific heat \( C_v/T \) can be plotted against \( T^2 \), i.e.,

\[
C_v/T = \gamma + \beta T^2
\]

in order to separate out the contribution of the ionic degrees of freedom (\( \beta T^3 \)) dominant at high temperatures. The coefficient \( \beta \) is related to \( \Theta \) as follows:

\[
\beta = \frac{9 N k_B}{\Theta^3} \int_0^{\Theta/T} \frac{e^z z^4 dz}{(e^z - 1)^2} 
\]

\[
\approx \frac{12 \pi^4 N k_B}{5 \Theta^3} (T \ll \Theta) .
\]
Here we note that experiments measure the specific heat at constant pressure, $C_p$, but we normally compare this result to $C_v$, since these two are almost identical in a solid.

The measured constant pressure specific heats $C_p$ of Ca$_{1-x}$Sr$_x$VO$_3$ below $\sim 15$ K are shown in Fig. 6. In the temperature range displayed in Fig. 6, it is clear that the data do not behave simply as Eq. 3. Thus, we have tried to fit the data to Eq. 3 below $T^2 < 2 \times 10^2 K^2$ ($T \sim 14$ K), where the identity seems more applicable. All the results of the least-square fits are summarized in Table III. We find that the value of $\gamma$, even in CaVO$_3$ ($x = 0$), is still not so enhanced as we discuss below ($m^*/m_b \simeq 2$), although these values are comparable to the La$_{1-x}$Sr$_x$TiO$_3$ system in the La rich phase except for $x < 0.05$. (The $\gamma$ values in the Ca$_{1-x}$Sr$_x$VO$_3$ system are much larger than that of the less correlated sodium metal $\sim 1$ mJ mol$^{-1}$K$^{-2}$.) The obtained Debye temperatures $\Theta$ are comparable to $\Theta \sim 300$ K deduced from the temperature of the phonon-drag peak of the Seebeck coefficient of CaVO$_3$, substantiating the result of our least-square fit to the specific heat data.

The effective masses compared to the band masses $m^*/m_b$ are defined as the ratios of the observed $\gamma$ to the $\gamma^{LDA}$. We plot the values of $m^*/m_b$ against $x$ with those deduced from the magnetic susceptibilities for comparison (Fig. 7).

From Fig. 7, we can also estimate the Sommerfeld-Wilson’s ratio $R_W$:

$$R_W \equiv \frac{\gamma^{LDA}}{\chi^{LDA}} \frac{\chi_P}{\gamma} = \left(\frac{m^*}{m_b}\right)^{\gamma} \left(\frac{m}{m_b}\right)^{\chi}$$

It is worthwhile emphasizing that $R_W$ is of order unity, implying that the electronic specific heat coefficient $\gamma$ is similarly enhanced to the Pauli paramagnetic susceptibility $\chi_P$. Furthermore, this means it is appropriate to assume a one-to-one correspondence between the quasiparticle excitations of this system and those of a free-electron gas.

For a non-interacting Bloch-electron system, $R_W = 1$. One of the possible reasons for $R_W \neq 1$ is a ferromagnetic fluctuation, which enters in $\chi_P$ as $\chi_P(\gamma) = (m^*/m_b)S$, where $S = (1 + F_0)\sim 3$ is called the Stoner enhancement factor including the 0-th asymmetric Landau parameter $F_0$. (For an isotropic free-electron system, $R_W$ becomes unity, because $F_0 = 0$.) In exchange-enhanced metals, i.e., a system with ferromagnetic fluctuations, $S$ plays an important role and $R_W$ becomes fairly large. However, this is not the case for the Ca$_{1-x}$Sr$_x$VO$_3$ system, since we have not observed any traces of ferromagnetic fluctuations.

The value of $R_W$ for Ca$_{1-x}$Sr$_x$VO$_3$ deduced from our experiments is $1.7 \sim 2$, as illustrated in Fig. 7, where the half values of $m^*/m_b$ deduced from the magnetic measurements are plotted for comparison. In strongly correlated electron systems, it has been argued that the value of $R_W$ becomes equal to 2 at $U/W = \infty$. Although there is a small deviation, $R_W \approx 2$ clearly indicates the importance of electron correlations in this system.

The deviation from $R_W = 2$ can be ascribed to the contribution of the electron-phonon interaction. It is known that this interaction contributes a factor $(1 + \lambda)$ to $\gamma$, but not to $\chi_P$. Hence, $R_W$ is modified to become $R_W(1 + \lambda)^{-1}$. From Fig. 7, we can approximately estimate $\lambda \sim 0.3$, so that the electron-phonon interaction in this system is fairly small. Furthermore, it should be noted that, for the higher orbital degeneracies,
TABLE III. Fitted parameters for the specific heat and deduced effective mass $m^*$ of Ca$_{1-x}$Sr$_x$VO$_3$. $\gamma^{LDA}$ has been calculated from $D(E_F)$ obtained by the LDA band calculation.$^{30,31}$ $m^*/m_b$ is defined as the ratio between $\gamma$ and $\gamma^{LDA}$.

| x  | $\Theta$ (K) | $\gamma$ (mJ mol$^{-1}$K$^{-2}$) | $\gamma^{LDA}$ (mJ mol$^{-1}$K$^{-2}$) | $m^*/m_b$ |
|----|-------------|-----------------|-----------------|-------------|
| 0.00 | 368.0 | 9.248 | 4.849 | 1.907 |
| 0.20 | 348.3 | 7.554 | 4.706 | 1.605 |
| 0.40 | 320.6 | 7.123 | 4.563 | 1.561 |
| 0.60 | 300.0 | 8.239 | 4.276 | 1.927 |
| 1.00 | 322.4 | 8.182 | 4.133 | 1.980 |

$R_W$ decreases towards unity in the limit of large orbital degeneracy.$^{39}$ Since the degeneracies of the $t_{2g}$ orbitals of the vanadium 3d electrons are not completely released in this Ca$_{1-x}$Sr$_x$VO$_3$ system, $R_W$ is not necessary to be equal to 2. However, there are experimental errorbars for the estimation of $\gamma$ values, the above argument needs to be further investigated.

Thus, we can conclude that $\sim 1.7 < R_W < \sim 2$ implies that electron correlations are strong in this system. Then, the question arises why is the enhancement of the effective mass so moderate, despite the presence of such large electron correlations?

The effective mass of a quasi-particle at the Fermi energy $E_F$ is defined in general as;

$$m^* = \left( \frac{1}{\hbar^2} \frac{d\varepsilon_k}{dk} \bigg|_{\vec{k} = \vec{k}_F} \right)^{-1}, \quad (4)$$

where $\varepsilon_k$ is quasi-particle energy that is given as a solution $\omega = \varepsilon_k$ of the equation

$$\omega = \varepsilon_k^o + \text{Re}\Sigma(\vec{k}, \omega), \quad (5)$$

where $\Sigma(\vec{k}, \omega)$ is the self-energy of the system in which all of the interaction effects are contained. $\varepsilon_k^o$ corresponds to the energy of a non-interacting Bloch electron. However, in this study, we regard $\varepsilon_k^o$ as the energy dispersion of a single-electron band obtained by the LDA band-calculation. Thereby, $\varepsilon_k^o$ gives a band mass $m_b$:

$$m_b = \left( \frac{1}{\hbar^2} \frac{d\varepsilon_k^o}{dk} \bigg|_{\vec{k} = \vec{k}_F} \right)^{-1}. \quad (6)$$

As is apparent from these definitions (Eqs. 3 and 4), $m^*$ and $m_b$ are given as tensors, but we assume here that the Fermi surface is isotropic and therefore $m^*$ is nothing but a scalar quantity. Using Eqs. 3 and 4, we deduce that the effective mass is given by the following expression:

$$\frac{m^*}{m_b} = \left| \frac{d\varepsilon_k^o}{dk} \bigg|_{\vec{k} = \vec{k}_F} \right| \times \left| \frac{\text{Re}\Sigma(\vec{k}, \omega)}{\omega} \bigg|_{\omega = E_F} \right| \times \left| \frac{d\varepsilon_k^o}{dk} \bigg|_{\vec{k} = \vec{k}_F} \right|,$$

where $m_\omega$ is called “$\omega$-mass” and $m_k$ is called “$k$-mass”.$^{40}$ If we consider only the on-site Coulomb interaction as the origin of the electron correlation and average out the fluctuation of the neighboring sites as in the limit of large lattice connectivity,$^{41}$ the self-energy depends only on the quasi-particle energy $\omega$, i.e., $\Sigma(\vec{k}, \omega) \equiv \Sigma(\omega)$. Then, the effective mass becomes (since $m_k/m_b = 1$):

$$\frac{m^*}{m_b} = \left( 1 - \frac{\partial\text{Re}\Sigma(\omega)}{\partial\omega} \bigg|_{\omega = E_F} \right)^{-1},$$

where $Z$ is the quasi-particle weight. Therefore, a critical enhancement of the effective mass due to strong electron correlations ($Z \to 0$) is inevitable at the MIT point.

However, in general, since the electron correlation is not necessarily confined to each atomic site, we may need to take into account the effect of the non-local Coulomb interaction, i.e., the self-energy should have a momentum-dependence.$^{42}$ Especially in the dynamical mean-field approach to the Mott transition,$^{43}$ the non-locality of the exchange interaction is not treated; therefore, we should introduce $\Sigma(\vec{k}_F, E_F)$, which is considerably different from zero.$^{20}$ The screening of the Coulomb potential can reduce $\Sigma(\vec{k}_F, E_F)$, because in well-screened systems such as conventional metals, the Coulomb potential is no longer long-range and the non-locality of the exchange interaction is small. However, in most of the perovskite-type TM oxides, the carrier density is fairly small, and this effect will be more significant in the vicinity of the MIT point.

We must assume therefore that, near the MIT point, the $\omega$-mass increases significantly reflecting $Z \to 0$; on the other hand, due to poor-screening, the contribution of the momentum-dependent self-energy becomes significant, resulting in a decrease of the $k$-mass. Thus, the critical enhancement of the effective mass, which is a product of the $\omega$-mass and the $k$-mass, can be suppressed in some conditions.$^{19}$ This is not only a plausible idea of explaining the behavior of the effective mass but also a model which provides a desirable picture of the reduction of the spectral intensity at the Fermi energy observed in the photoemission and inverse-photoemission spectroscopies.$^{19,20,43}$

In summary, in order to obtain a comprehensive understanding of the metallic state near the Mott transition,
we should note that the momentum-dependence of the self-energy plays an important role in this region.

D. Electric resistivity

The electric resistivities collected on both heating and cooling cycles between 350 K and 4 K show no difference within the experimental accuracy. In some cases, the resistivity shows clear dependence on the crystallographic alignments of the experiment; \textit{i.e.}, when the measuring current flows parallel to the [100]-axis of the pseudocubic perovskite, the resistivity is different from that when the current flows along the [110]-axis. This anisotropy, however, is not temperature-dependent. Whenever we observe such anisotropy, we normalize each data set to the residual resistivity $\rho_0$, and the resulting curves fit each other completely.

The scaling factor $c \equiv \rho^{[110]}(T)/\rho^{[100]}(T)$, varies from $\sim 1.1$ to $\sim 1.5$. However there seems to be neither a systematic relation between $c$ and the Sr content $x$, nor consistency among the different sets of the measurements for the samples with the same value of $x$.

Thus, we consider that the observed anisotropy is not due to any particular feature of the electronic structure of the system. Similar behavior has been reported in the resistivity of the single crystal CoSi$_2$ with cubic C1 structure,\cite{44} and also high-purity cubic Al single crystal.\cite{45} In the former material, it was pointed out that the anisotropy can be attributed to an extrinsic origin, \textit{e.g.}, point defects and/or dislocations that appeared during crystal growth, though no trace of such defects has yet been observed.\cite{44} It has been argued that, in the case of the Al single crystal, a model calculation for (211) dislocations predicts an anisotropy of electrical resistivity compatible with experiment.\cite{46} Therefore, we suggest that the anisotropy in our resistivity measurements may also be caused by the presence of a small amount of defects and/or dislocations.\cite{47} Despite this undesirable artifact, if we make the size of the rectangular parallelepiped as small as $2 \times 0.5 \times 0.3 \text{mm}^3$, the absolute values of the electric resistivity data can be reproduced within the $\pm 15\%$ error bar (the temperature dependence is completely reproducible as mentioned above) irrespective of the direction of the measuring current. With all these considerations, the data were collected as shown in Fig. 8.

At first sight, all the data seem to be well expressed by the relation $\rho = \rho_0 + AT^2$ for the measured temperature range. However, when we try to fit the observed resistivity using this expression, we cannot fit the data over the entire temperature range from 4 K to 350 K using a single value of the coefficient $A$. Therefore we assume that the resistivity is expressed by $\rho_0 + AT^2$ plus an additional term.

Firstly, we consider here that the $AT^2$ term is due to electron-phonon scattering. It has been suggested, especially in strongly-coupled superconductors, that the $AT^2$ term is due to the breakdown of the momentum-conservation law in the electron-phonon scattering process.\cite{48} Here the coefficient $A$ is shown to be related to both the residual resistivity $\rho_0$ and the Debye temperature $\Theta$:

$$A = \alpha \times \frac{\rho_0}{\Theta^2} \quad (7)$$

with $\alpha$ varying from $\sim 0.01$ to $\sim 0.1$. However, the $A$ values in the Ca$_{1-x}$Sr$_x$VO$_3$ system, which are roughly estimated as $\sim 1 \times 10^{-9} \text{\Omega cm/K}^2$, are three orders larger than

$$\alpha \times \frac{\rho_0}{\Theta^2} = \alpha \times \left(\frac{1 \times 10^{-5} \text{\Omega cm}}{\sim 5 \times 10^2 \text{K}^2}\right) = \sim 4 \times 10^{-12} \text{\Omega cm/K}^2,$$

even if we assume the largest value of $\alpha \sim 0.1$. (Here we used the Debye temperature estimated from the specific heat measurement.) Furthermore, Gurvitch has discussed that a strong electron-phonon interaction is insufficient for the $T^2$ law; the simultaneous presence of strong coupling and disorder is also necessary.\cite{49} He has also pointed out that, in some cases, Eq. 6 is not applicable; \textit{i.e.}, there is an empirical condition for the appearance of the $T^2$ law:

$$(\lambda - 0.7) \times \rho_0 > \sim 13 \text{\mu\Omega cm},$$

where $\lambda$ is the electron-phonon coupling constant. In the Ca$_{1-x}$Sr$_x$VO$_3$ system, however, $\lambda$ is at largest $\sim 0.3$ as discussed in Sec. 11, and $\rho_0$ is $\sim 1 \times 10^{-5} \text{\Omega cm}$. Hence, the last formula is not satisfied. (In the first place, even the value of $\lambda$ is smaller than 0.7.) Following these arguments, it appears unlikely that the $T^2$-dependent resistivity in Ca$_{1-x}$Sr$_x$VO$_3$ arises from electron phonon scattering. However, this kind of contribution to the $T^2$ term.

![Fig. 8. Electric resistivities of the Ca$_{1-x}$Sr$_x$VO$_3$ single crystals for $x = 0.00, 0.25, 0.50, 0.70, 1.00$. For each data set, the minimum resistivity at $\sim 4 \text{K}$ has been subtracted as the residual resistivity $\rho_0$.](image-url)
is not completely neglected and will be discussed again below.

An alternative and more likely origin of the $T^2$ term is electron-electron scattering in the presence of the umklapp process. Let us consider here the resistivity as modeled by a three-component expression of the form:

$$\rho = \rho_o + A T^2 + \rho_{e-ph}(T)$$

where $\rho_o$ is a temperature-independent background contribution due to static disorder, $\rho_{e-e}(T) \equiv A T^2$ is the electron-electron scattering. By the line-shape analysis such as is shown in Fig. 9, we found that the third term $\rho_{e-ph}(T)$ is well represented by the classical Bloch-Grüneisen formula for electron-phonon scattering with $n = 5$, developed for an isotropic Fermi surface and a simple phonon spectrum:

$$\rho = \rho_o + A T^2 + 4\kappa T^n \int_0^{\Theta/T} \frac{e^{z^n} - 1}{(e^z - 1)^2} \, dz \quad (n = 5) \quad (8)$$

![Fig. 9. Electric resistivity of Ca$_{0.5}$Sr$_{0.5}$VO$_3$ against temperature $T$ (dots). The solid line represents Eq. (8) while the broken line represents Eq. (8) without the Bloch-Grüneisen term.](image)

We have done a least-square fit to all the data using Eq. (8) and the obtained parameters are summarized in Table IV and also in Fig. 10. If we accept $\sim \pm 15\%$ error bar, we can conclude that each of the fitted parameters shows systematic behavior as a function of Sr content $x$.

$\rho_o$ shows a maximum at $x = 0.5$. This reflects that the system has the maximum amount of randomness at that composition.

We note that our effective transport Debye temperature $\Theta \sim 700 K$ does not sound physical. However it is not necessary for the transport $\Theta$ to be equal to the thermodynamic value $\Theta \sim 350 K$ obtained from the specific heat measurements. This is because the transport Debye temperature involves only the acoustic modes that interact with the electrons, whereas the thermodynamic Debye temperature considers all types of phonons.

The values of $\kappa$ and $\Theta$ show a minimum at $x = 0.5$, indicating that the lattice becomes softest at this composition. The electron-phonon coupling constant $\lambda$ is related to both $\kappa$ and $\Theta$ as follows:

$$\lambda \propto \frac{\omega_p^2}{\Theta^2} \kappa,$$

where $\omega_p$ is the plasma frequency of the conduction electrons. Makino et al. reports in the following paper that the variation of $\omega_p$ in going from SrVO$_3$ to CaVO$_3$ is systematic but very small, and the variation of $\lambda$ inferred from the Sommerfeld-Wilson’s ratio $R_W$ is also small. Thus we can roughly estimate that $\kappa \sim \Theta^2$. This is consistent with the behaviors shown in Fig. 10.
It is surprising that the contribution of the electron-electron scattering, which is in general dominant at very low temperature, is significantly large even at room temperature. In Ca$_{0.5}$Sr$_{0.5}$VO$_3$,

$$\rho_{e-e}(300\,K) : \rho_{e-ph}(300\,K) \approx 2 : 1.$$ 

This is further evidence that the electron correlations are significantly large in this system. The coefficient $A$ should, then, reflect the enhancement of the effective mass of the quasi-particles due to this electron correlation. The resistivity due to electron-electron (i.e., quasiparticle – quasiparticle) scattering can be crudely but quantitatively expressed as follows:

$$\rho_{e-e}(T) = \frac{m^* v_F}{e^2 n^{2/3}} \left( \frac{k_B T}{E_F} \right)^2 = \frac{4k_B^2 m^*}{\hbar^2 e^2 n^{2/3}} T^2 = AT^2,$$

where $v_F = \hbar k_F/m^*$, $E_F = \hbar^2 k_F^2/(2m^*)$, and we have assumed the scattering time $\tau$ is equal to the life time of the thermally activated quasiparticle $\tau^{-1} = v_F n^{1/3} E_F^{-1} Z^{-1} \text{Im}\Sigma \approx v_F n^{1/3} (m^*/m_b)(k_B T/E_F)^2$. Hence, the coefficient $A$ is proportional to the quadratic of the effective mass $m^*$. The obtained value of $A$ increases systematically in going from $x = 1$ to $x = 0.25$; this may correspond to the increase of $m^*$. However there seems to be a rapid decrease between $x = 0.25$ and $x = 0$ which is not consistent with the behavior of $m^*$. This is not obviously explained by the considerably large error arising from the quality of the sample ($\pm 15\%$).

In Fig.10 (top), we also plot the value of $A$ deduced from the Pauli paramagnetic susceptibility $\chi_P$ under a few reasonable assumptions: we use a Sommerfeld-Wilson’s ratio $R_W = 2$ to estimate the electronic specific heat $\gamma$ from $\chi_P$, since $R_W$ is almost equal to 2 in this system. The obtained $\gamma$ corresponds to the electronic specific heat which is not affected by the electronphonon interaction. Then we use the Kadowaki-Woods ratio $A/\gamma^2$, which is a measure of the electron correlation, of the same value as that of the heavy fermion systems, i.e., $A/\gamma^2 = 1.0 \times 10^{-5} \mu\Omega\text{cm}\,\text{mol}^2\,\text{K}^2\,(\text{ml})^{-2}$, and deduced the value of $A$. The resulting $A$ values are compared to the experimentally observed values (Fig. 10, top).

Since the above assumptions for the Sommerfeld-Wilson’s ratio and the Kadowaki-Woods ratio in this system seem to be fairly appropriate, we can safely say that the $AT^2$ term in the resistivity of the end members CaVO$_3$ ($x = 0$) and SrVO$_3$ ($x = 1$) is attributed to only the electron-electron scattering. For the other solid-solutions ($0 < x < 1$), there must be other contributions to the $AT^2$ term. The most probable candidate of this additional contribution of the $T^2$ term is the interference between the elastic electron scattering and the electron-phonon scattering, which has been recently investigated by Ptitsina et al.\textsuperscript{53} This effect must be proportional to the residual resistivity, and our data seems to support the scenario.

On the other hand, however, we know that the Kadowaki-Woods ratio is not necessarily equal to the above value. Then, there are several other reasons to be considered for the observed $x$-dependence of $A$. We must consider a possible contribution from the modification of the Fermi surface. Since $A$ is not only proportional to $m^* \cdot T^2$ but also to $k_F^{-3}$, a variation of the shape of the Fermi surface due to the orthorhombic distortion may lead to changes in $A$. In passing, as we apply pressure to CaVO$_3$, the value of $A$ tends to decrease,\textsuperscript{36,54} though it has not yet been determined how the lattice constants change under pressure. We should also remark that samples around $x = 0.25$ have a tendency to show the smallest spectral weight at the Fermi energy as observed in the recent studies of the photoemission spectroscopy\textsuperscript{55} and the inverse photoemission spectroscopy of the Ca$_{1-x}$Sr$_x$VO$_3$ single crystals.\textsuperscript{56} This might be related to the hybridization between the V 3d $t_{2g}$ orbitals and the O 2p $\sigma$ orbitals. Okimoto et al. calculated a distortion-induced admixture between those orbitals,\textsuperscript{57} and Lombardo et al. discussed a possible scenario involving spectral weight transfer in the Ca$_{1-x}$Sr$_x$VO$_3$ system due to charge transfer.\textsuperscript{58} This distortion-induced charge transfer may explain the strange revival of the quasi-particle weight in the region close to CaVO$_3$, and this hybridization may also explain the $x$-dependence of the value of $A$, although this should be consistent with the monotonic increase of the effective mass toward CaVO$_3$ as estimated from the Pauli paramagnetism. Finally, the contribution of the momentum-dependence of the self-energy, which becomes significant in the region closer to CaVO$_3$,\textsuperscript{19,20} is also an intriguing candidate to explain the behavior of $A$. Apparently, with a large momentum-dependence of the self-energy, it is no longer necessary that $A$ is proportional to $m^* \cdot T^2$. These

| $x$ | $\rho_0$ ($\Omega$cm) | $A$ ($\Omega$cm/K$^2$) | $\kappa$ ($\Omega$cm K) | $\Theta$ (K) |
|-----|------------------|----------------------|------------------------|--------|
| 0.00 | $8.668 \times 10^{-6}$ | $5.911 \times 10^{-10}$ | 0.114 | 793.5 |
| 0.25 | $1.319 \times 10^{-5}$ | $9.118 \times 10^{-10}$ | 9.476 $\times 10^{-2}$ | 722.2 |
| 0.50 | $1.827 \times 10^{-5}$ | $7.900 \times 10^{-10}$ | 7.441 $\times 10^{-2}$ | 647.3 |
| 0.70 | $8.656 \times 10^{-6}$ | $6.796 \times 10^{-10}$ | 8.073 $\times 10^{-3}$ | 811.5 |
| 1.00 | $6.205 \times 10^{-6}$ | $4.208 \times 10^{-10}$ | 0.121 | 866.3 |
We have succeeded to prepare single crystals of the metallic alloy system Ca_{1-x}Sr_xVO_3 for the first time, as far as we are aware. The system has nominally one 3d electron per vanadium ion; as we substitute a Ca^{2+} ion for a Sr^{2+} ion, the band width W decreases due to the buckling of the V-O-V bond angle from ~180° for SrVO_3 to ~160° for CaVO_3, which is almost equal to the analogous 3d^1 insulator LaTiO_3. Thereby, it is reasonable to consider that CaVO_3 is close to the boundary of MIT. The Sommerfeld-Wilson’s ratio R_W ≃ 2, the Kadowaki-Woods ratio A/γ^2 lies in the same region as the heavy Fermion compounds, and there is a large contribution from electron-electron scattering to the resistivity even at room temperature. These features are considered to provide strong evidence of the large electron correlations in this system. However, the effective mass obtained by the thermodynamic (γ) and magnetic (χ_P) measurements show only a moderate increase in going from SrVO_3 to CaVO_3, instead of the diverging behaviors expected from the Brinkmann-Rice picture.

The elaborate band-width control in Ca_{1-x}Sr_xVO_3 has elucidated that the mass-enhancement due to the reduction of the band width is not so large, even though the system shows some fingerprints of a large electron correlation. Accordingly, we suggest that these seemingly contradicting metallic properties observed in this system can be explained by considering the effect of non-local electron correlations, i.e., the momentum-dependent self-energy.

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17. R. D. Shannon, Acta Crystallogr. A 32, 751 (1976).

18. The GdFeO$_3$ type lattice distortion possibly causes anisotropy and affects electron-phonon interactions. However, in this system, these contributions are not predominant for the metallic properties, as revealed by our measurements and the following discussion. This could also justify the metallic Ca$_{1-x}$Sr$_x$VO$_3$ alloy as an ideal compounds.

19. I. H. Inoue, I. Hase, Y. Aiura, A. Fujimori, Y. Haruyama, T. Maruyama, and Y. Nishihara, Phys. Rev. Lett. 74, 2539 (1995).

20. K. Morikawa, T. Mizokawa, K. Kobayashi, A. Fujimori, H. Eisaki, S. Uchida, F. Iga, and Y. Nishihara, Phys. Rev. B 52, 13711 (1995).

21. M. J. Rozenberg, I. H. Inoue, H. Makino, F. Iga, and Y. Nishihara, Phys. Rev. Lett. 76, 4781 (1996).

22. H. Makino, S. Onari, and I. H. Inoue, following paper, Phys. Rev. B (submitted).

23. I. H. Inoue, K. Morikawa, H. Fukuchi, T. Tsujii, F. Iga, and Y. Nishihara, Jpn. J. Appl. Phys. 32, 451 (1993).

24. Very recently, we have obtained preliminary specific heat data for single crystals, which are almost similar to those for the poly crystals.

25. M. Ishikawa, Y. Nakazawa, T. Takabatake, A. Kishi, R. Kato, and A. Maesono, Solid State Comm. 66, 201 (1988).

26. Y. Ueda, private communication.

27. J. C. Phillips, Phys. Rev. B 46, 8542 (1992).

28. A. Fukushima, F. Iga, I. H. Inoue, K. Murata, and Y. Nishihara, J. Phys. Soc. Jpn. 63, 409 (1994).

29. N. Shirakawa, K. Murata, H. Makino, F. Iga, and Y. Nishihara, J. Phys. Soc. Jpn. 64, 4824 (1995).

30. I. Hase, private communication: the shape of the DOS is seen in Ref. 22. See also, K. Takegahara, J. Electron Spectrosc. Relat. Phenom. 66, 303 (1994).

31. For $D(E_F)$, we have used the LDA DOS at $E_F$ for CaVO$_3$ and SrVO$_3$, and have simply made a linear interpolation for the intermediate Sr/Ca stoichiometries.

32. J. H. Van Vleck, in The Theory of Elecronic and Magnetic Susceptibilities (Oxford University Press, United Kingdom, 1932).

33. This term corresponds to the Van Vleck paramagnetism in insulating materials, and becomes large when the “quenching” of the orbital angular moment is not sufficient. Moreover, this term can be enhanced by the electron correlation, since electron correlations change the electron configuration as well as the crystal field, and the Van Vleck term cannot be treated by a one-body approximation. The $x$-dependence of the fourth term in the Ca$_{1-x}$Sr$_x$VO$_3$ system is still an open question: see e.g., H. Kontani and K. Yamada, J. Phys. Soc. Jpn. 65, 172 (1996).

34. J. P. Pouget, H. Launois, T. M. Rice, P. Derrier, A. Gossard, G. Villeneuve and P. Hagenmuller, Phys. Rev. B 10, 1801 (1974).

35. A bump which appears around 2K in the specific heat can be subtracted by assuming Schottky contribution of $\sim 0.2\%$ impurities. This amount of impurities is consistent with that deduced from the magnetic Curie-Weiss contribution.

36. J.-S. Zhou and J. B. Goodenough, Phys. Rev. B 54, 13393 (1996).

37. K. Wilson, Rev. Mod. Phys. 47, 773 (1975).

38. P. Nozières, J. Low Temp. Phys. 17, 31 (1974).

39. A. Yoshimori, Prog. Theor. Phys. 55, 67 (1976).

40. H. R. Glyde, S. I. Hernadi, Phys. Rev. B 28, 141 (1983); C. W. Greef, H. R. Glyde, and B. E. Clements, ibid 45, 7951 (1992).

41. For example, the Hubbard model in the limit of large lattice connectivity: A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996), and the references therein.

42. Even in the case where only the on-site Coulomb interaction is included in the model Hamiltonian, the self-energy can be non-local (momentum-dependent). For example, the effect of antiferromagnetic fluctuation due to Fermi surface nesting has already been discussed in the literature: A. Kampf and J. R. Schrieffer, Phys. Rev. B 41, 6399 (1990); M. Langer, J. Schmalian, G. Grabowsky, and K. H. Bennemann, Phys. Rev. Lett. 75, 4508 (1995); J. J. Deisz, D. W. Hess, and J. W. Serene, Phys. Rev. Lett. 76, 1312 (1996).

43. A. Fujimori, K. Morikawa, T. Mizokawa, T. Saitoh, M. Nakamura, Y. Tokura, I. Hase, and I. H. Inoue, in Ref. 4, p. 174.

44. T. Hirano and M. Kaise, J. Appl. Phys. 68, 627 (1990).

45. E. Hashimoto, Y. Ueda, H. Tamura, and T. Kino, J. Phys. Soc. Jpn. 62, 4178 (1993).

46. B. R. Watts, J. Phys. F 17, 1703 (1987).

47. When the rate of crystal growth is fairly large, it is hard to explain this process on a plane by plane basis. However, if the crystal contains a screw dislocation, it is never necessary to nucleate a new plane, as the local planar structure can wind endlessly about the screw dislocation. This kind of process might be realized in some cases during our crystal growth.

48. S. Koshino, Prog. Theor. Phys. 24, 1049 (1960); ibid 30, 415 (1963); P. L. Taylor, Phys. Rev. 135, A1333 (1964); Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 50, 1107 (1966); D. H. Damon, M. P. Mathur, and P. G. Klemens, Phys. Rev. 176, 876 (1968); H. Takayama, Z. Phys. 263, 329 (1973); P. J. Cote and L. V. Meisel, Phys. Rev. Lett. 39, 102 (1977); F. J. Okkawa, J. Phys. Soc. Jpn. 44, 1105 (1978).

49. M. Gurvitch, Phys. Rev. Lett. 56, 647 (1986).

50. B. Bucher, P. Steiner, J. Karpinski, E. Kaldis, and P. Wachter Phys. Rev. Lett. 70, 2012 (1993).
In strongly correlated electron systems, the electron-electron scattering is the dominant process to induce the decoherence of the wavefunction, which thus determines the relaxation time $\tau$ under the presence of the umklapp process. Then, the quasi-particle – quasi-particle scattering time is given by $\tau^{-1} \propto Z^{-1} \text{Im} \Sigma$, where $Z$ is the quasi-particle weight and $\Sigma$ is the self-energy.

K. Kadowaki and S. B. Woods, Solid State Commun. 58, 507 (1986).

N. G. Ptitsina, G. M. Chulkova, K. S. Il’in, A. V. Sergeev, F. S. Pochinkov, E. M. Gershenzon, and M. E. Gershenson, Phys. Rev. B 56, 10089 (1997), and the references therein.

When we apply a hydrostatic pressure up to 8 GPa to CaVO$_3$, the resistance at room temperature decreases $\sim 30\%$ monotonically: F. Iga, unpublished.

I. H. Inoue, H. Makino, I. Hase, Y. Aiura, Y. Haruyama, and Y. Nishihara, Physica B 230-232, 780 (1997).

D. D. Sarma and K. Maiti, private communication.

Y. Okimoto, T. Katsufuji, Y. Okada, T. Arima, Y. Tokura, Phys. Rev. B 51, 9581 (1995).

P. Lombardo, J. Schmalian, M. Avignon, K. H. Bennemann, Physica B 230-232, 415 (1997).