Orbital-Ordering Transition in Sr$_2$VO$_4$

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Temperature-dependent dc susceptibility and x-ray powder diffraction on a pure tetragonal sample of Sr$_2$VO$_4$ show an antiferromagnetic orbital-ordering transition at $T_{00} = 97$ K, in which the occupied orbitals lie along the c axis. The unusual broadening of the x-ray Bragg peaks throughout the orbital-ordering transition temperature region indicates that this process occurs in stages, and the onset of short-range orbital ordering occurs at $T_1 \approx 122$ K. The study of the order parameter associated with this transition by analyzing the spontaneous strain results in a critical exponent $\beta = 0.35(2)$ consistent with 3D Heisenberg behavior. These results experimentally confirm the orbital-ordering state in Sr$_2$VO$_4$ predicted by first-principles calculations using combinations of the local-density approximation and the GW method.

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Layered perovskites are well-known to exhibit various intriguing physical phenomena; two celebrated examples are high-temperature $d$-wave superconductivity in the cuprates La$_{2-x}$Sr$_x$CuO$_4$ [1] and low-temperature (LT) $p$-wave superconductivity in Sr$_2$RuO$_4$ [2]. The search for exotic physics in $s = 1/2$ systems has led to the synthesis of analogous materials which retain the K$_2$NiF$_4$ structure. Sr$_2$VO$_4$, which has a similar $s = 1/2$ $V^{4+}$ (3$d^1$) state as Cu$^{2+}$ (3$d^9$) and Ru$^{4+}$ (4$d^5$), has been an elusive target for study due to the difficulty in producing single phase samples. Previous studies on the tetragonal phase have shown that (i) a magnetically ordered ground state appears below 45 K, with a Néel temperature that is sensitive to sample quality [3,4], and (ii) thin films have an activation energy of ~90 meV, which suggests that a very small Mott gap exists in Sr$_2$VO$_4$, and low amounts of La doping easily induce the metallic phase [5,6]. The impetus to study the tetragonal phase of Sr$_2$VO$_4$ originates from a recent first-principle calculation which predicted that a nontrivial orbital-stripe order emerges at ~100 K in Sr$_2$VO$_4$, and the sample is close to a metal-insulator transition from the localized electron side of the phase diagram [7]. The energy scale of ~100 K plays a role in the physics of the related materials La$_{2-x}$Sr$_x$CuO$_4$ and Sr$_2$RuO$_4$—the former has a structural transition [8] and the formation of a pseudogap as a function of doping [9], and the latter has a subtle $c/a$ ratio change near 100 K [10].

Until now, no experimental evidence has been presented in the literature of the predicted orbital-ordering transition in tetragonal Sr$_2$VO$_4$. One possible reason for this is due to the difficulty in synthesizing high quality single phase Sr$_2$VO$_4$ to show the intrinsic properties. In this Letter we detail the synthesis of single phase tetragonal Sr$_2$VO$_4$ samples to search for signatures of orbital ordering. The magnetic and low-temperature structural data on this sample clearly shows a transition at 97 K, and the stages of this transition are well characterized.

The sample Sr$_4$V$_2$O$_9$ was first prepared by solid state reaction in air of the appropriate mixture of SrCO$_3$ and V$_2$O$_5$ at 1073 K for 60 hours. Polycrystalline Sr$_2$VO$_4$ compound was made by reduction of Sr$_4$V$_2$O$_9$ under a H$_2$ flow at 1323 K for 100 hours, with several grindings of the sample. The x-ray powder diffraction (XRD) patterns were recorded by a HUBER imaging plate Guinier camera 670 using Cu $K\alpha_1$ radiation (1.54059 Å) with a Ge monochromator. Data were collected in steps of 0.005° with temperatures down to 9 K obtained with a closed cycle He fridge. The data was obtained by warming up with a temperature ramp rate of 6 K/hour and a dwell time of 20 minutes/temperature. XRD data was fit from the Rietveld refinement by using the program FullProf with typical $R_p \approx 7.0\%$, $R_{wp} \approx 8.0\%$, and $\chi^2 \approx 1.8$. Direct current magnetic susceptibility was measured with a Quantum Design SQUID magnetometer after cooling in either zero field or in a field of 2000 Oe.

The room-temperature XRD pattern [Fig. 1(a)] shows that the sample is single phase with a tetragonal $I4/mmm$ structure. The lattice parameters are $a = 3.8347(1)$ Å and $c = 12.5309(2)$ Å. Compared to the reported data [$a = 3.8341(1)$ Å and $c = 12.57(1)$ Å], the lattice parameter $a$ is similar, but the lattice parameter $c$ is slightly shorter [3]. The major difficulty in the synthesis of tetragonal Sr$_2$VO$_4$ is its metastability. At high temperatures the tetragonal phase will (a) transform to an orthorhombic phase above 1373 K, which shows a broad peak at around 60 K in the dc magnetization [11]; (b) lose SrO to form Sr$_3$V$_2$O$_7$, which has a similar $a$ axis but a longer $c$ axis compared to Sr$_2$VO$_4$ [3]. It is necessary to heat the sample at low temperatures (below 1373 K) and for long periods of time to obtain the pure tetragonal phase.

Several features are noteworthy from the temperature dependence of the susceptibility ($\chi$), Fig. 2: (i) the fits above 200 K with the Curie-Weiss law gives a Curie-Weiss constant $\theta = -1100$ K and $\mu_{eff} = 5.0\mu_B$, which are not...
Furthermore, \( \chi \) deviates from the linear behavior below 200 K. (ii) the susceptibility begins a sharp drop at \( T_2 = 104 \) K, followed by an upturn at \( T_{OO} = 97 \) K; (iii) the zero-field–cooled and field-cooled curves begin to diverge at \( \sim 70 \) K [inset of Fig. 2(a)]. This behavior is typical for weak ferromagnetism. The large Curie-Weiss constant and \( \mu_{\text{eff}} \) of \( \text{Sr}_2\text{VO}_4 \) have a likely origin in the weak temperature dependence of the dc susceptibility, which is more characteristic of strongly enhanced Pauli paramagnetism than the usual Curie-Weiss behavior for the localized \( \text{V}^{4+}(3d^1) \) state. This kind of enhanced Pauli paramagnetism is typical for strongly correlated \( 3d \) electron systems sitting on the edge of metal-insulator transitions. For example, the perovskites LaTiO\(_3\) (\( 3d^1 \) electron on the localized side) and CaVO\(_3\) (\( 3d^1 \) electron on the itinerant side) are both in close proximity to a metal-insulator transition and show enhanced Pauli paramagnetism at high temperatures [12,13]. Furthermore, the activation energy for the Mott insulator LaTiO\(_3\) is 35 meV [12], which is comparable to the activation energy obtained from the thin film sample of \( \text{Sr}_2\text{VO}_4 \). It is likely that \( \text{Sr}_2\text{VO}_4 \) lies close to a metal-insulator transition on the localized electron side. The drop of the susceptibility around 100 K reported here is at the same temperature of the predicted orbital-ordering transition from first-principle local-density approximation physically meaningful for the localized \( \text{V}^{4+}(3d^1) \) ion.

GW calculations [7]. The drop is also similar to that observed in the orbital-ordering transition in \( \text{La}_4\text{Ru}_2\text{O}_{10} \) [14] or spin-singlet formation in MgTi\(_2\)O\(_4\) [15], both of which are accompanied by structural distortions at low temperatures.

Low-temperature XRD experiments were completed to investigate this possible orbital-ordering transition in \( \text{Sr}_2\text{VO}_4 \). Below 122 K, several Bragg peaks broaden in \( Q \) and become split. In particular, the (200) peak can be fit to two Lorentzians in the temperature range between 122 and 94 K [Fig. 3(a)]. Below 94 K, this peak can be fit to only one Lorentzian. This can have two possible origins: (i) there are two coexisting tetragonal phases between 122 and 94 K, or (ii) an orthorhombic phase exists between 122 and 94 K, which evolves into a different tetragonal phase below 94 K. We have checked the intermediate phase to solve for the most probable orthorhombic space group (\( \text{Ima}2 \)), and we have also tried to model the split reflections based on this choice. Although we cannot rule out the possibility of an orthorhombic phase with our powder diffraction data, we cannot observe the splitting of other peaks in the range of 94–122 K such as (121) or (211) that would occur in the orthorhombic space group. Furthermore, we also note that there should be a large splitting between the (118) and (220) peaks within the range of 122 to 94 K. Since we only see an appreciable splitting at much lower temperatures (due to the lattice parameter change upon cooling), we conclude that the former possibility, of two coexisting tetragonal phases, is more likely. The physical reason for the split of the (118)/(220) peaks in Fig. 3(b) below 94 K is the rapid
expansion of the \textit{c} axis and contraction of the \textit{a} axis. This leads to a rise in the \textit{c}/\textit{a} ratio typical in orbital-ordering transitions [Fig. 4(d)] [16].

The integrated area of each of the (200) Bragg peaks around 100 K was used as a measure of the volume fraction of each phase [Fig. 4(b)]. Within the region of 94–122 K, the total area of the two peaks was constant, and the evolution of the new phase is correlated with the drop in the dc susceptibility. The appearance and coexistence of the new phase suggests that the system is near a first order transition and is reminiscent of other structural phenomena in orbitally ordered systems such as La$_4$Ru$_2$O$_{10}$ [14] and the perovskite manganites. In manganites, the orbital-ordering state induced by the Jahn-Teller distortion of the MnO$_6$ octahedra always occurs in stages [16,17]. The polycrystalline data here cannot completely exclude the orthorhombic distortion in the system. Single crystalline XRD data should be studied in the future.

Because of the difficulty in extracting the bond lengths from XRD data, we cannot make any statements about the distortions on the V-O tetrahedra at the transition, although there is a tendency toward further distortion of the V-O octahedra by the elongation along the fourfold symmetry axis. There is no change in crystallographic symmetry across the structural transition in SrV$_2$O$_4$. This is different from the high-temperature superconductor La$_{2-x}$Sr$_x$CuO$_4$, in which a structural transition from the tetragonal to orthorhombic phase is obtained by tilting the copper-oxygen octahedra about either the (110) or (110) axes [8]. In Sr$_2$VO$_4$, the 3d orbitals are split into $e_g$ and $t_{2g}$ orbitals, and the $t_{2g}$ orbitals are further split into the \textit{xy}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Temperature & Atom & \textit{x} & \textit{y} & \textit{z} & \textit{B} (Å$^2$) \\
\hline
122 K & Sr & 0 & 0 & 0.3551(1) & 1.73(4) \\
& V & 0 & 0 & 0 & 1.80(7) \\
& O(1) & 0.5 & 0 & 0 & 1.80(1) \\
& O(2) & 0 & 0 & 0.1546(52) & 1.70(2) \\
& V-O(1) & 1.9137(1) (Å) & & & & \\
& V-O(2) & 1.94(6) (Å) & & & & \\
94 K & Sr & 0 & 0 & 0.3550(1) & 1.38(4) \\
& V & 0 & 0 & 0 & 1.65(5) \\
& O(1) & 0.5 & 0 & 0 & 1.50(1) \\
& O(2) & 0 & 0 & 0.1558(56) & 1.60(2) \\
& V-O(1) & 1.9103(1) (Å) & & & & \\
& V-O(2) & 1.95(6) (Å) & & & & \\
\hline
\end{tabular}
\caption{Crystallographic parameters and selected bond lengths for Sr$_2$VO$_4$ at 122 K [\textit{a} = 3.8274(1) Å, \textit{c} = 12.5225(2) Å] and 94 K [\textit{a} = 3.8256(2) Å, \textit{c} = 12.5308(2) Å].}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{(color). Temperature dependencies of (a) lattice parameter \textit{c}, (b) lattice parameter \textit{a}. Open circles are experimental data and the red lines are fits using Eqs. (1) and (2); The lattice parameters are calculated from the Rietveld refinement by FullProf. (c) \textit{c}/\textit{a} ratio; (d) phase fraction of HT-Sr$_2$VO$_4$ and LT-Sr$_2$VO$_4$ determined by refining the XRD data, and volume. Inset of (a) and (b): $\Delta c$ and $\Delta a$ proportional to ($1 - T/T_{OO}$) plotted in log-scale.}
\end{figure}
orbital and degenerate \( yz \) and \( xz \) orbitals due to the twodimensionality of the tetragonal structure, Fig. 1(c). The abrupt expansion of the \( c \) axis and shrinkage of the \( a \) axis at 94 K clearly reflect an increased occupancy of the \( d_{xz}/d_{yz} \) orbitals and a decreased occupancy of the \( d_{xy} \) orbital. Because of the repulsion between \( V \) and \( O \) orbitals, the orbital axis is expected to lie in the \( c \) direction. Here the abrupt change of the \( c/a \) ratio can be contrasted with the subtle increase of the \( c/a \) ratio around 100 K in \( \text{Sr}_2\text{RuO}_4 \). There is no structural transition down to 0.3 K for \( \text{Sr}_2\text{RuO}_4 \) but a subtle increase of the \( c/a \) ratio around 100 K [10], which could be the reason for the crossover from non-metallic to metallic behavior exhibited from \( \rho_c \) near 130 K [2]. The study of \( \text{Sr}_2\text{Ir}_{2-x}\text{Ru}_x\text{O}_4 \) also highlighted the relation between the \( c/a \) ratio and the transition from a localized to itinerant electronic state [18].

From the combination of the XRD and susceptibility results, the stages of the orbital-ordering transition in \( \text{Sr}_2\text{VO}_4 \) can be well characterized as (i) the mixed phase region begins at \( T_1 = 122 \text{ K} > T_{\text{OO}} = 97 \text{ K} \), which suggests that short-range orbital ordering appears at high temperatures; (ii) at \( T_2 = 104 \text{ K} \), when the fraction of the LT phase is at 40%, the susceptibility begins to drop, which shows the antiferromagnetic character of the orbital-ordering state. The transition is complete by 94 K; (iii) the expansion of the \( c \) axis is essentially complete at 70 K, below which the system shows weak ferromagnetism.

The evolution of the lattice parameter around \( T_{\text{OO}} \) is reminiscent of an order parameter. In particular, the rise of the \( c \) parameter and drop of \( a \) parameter as a measure of spontaneous strain is similar to what is seen in other orbital-ordering [19] or spin-Peierls [20] transitions. In order to extract the spontaneous strain from the relative changes in lattice constant, the lattice parameters above the transition temperature are fit to a suitable polynomial and taken to represent the background. Because of the intermediate temperature region above \( T_{\text{OO}} \) (100–300 K), the temperature dependencies of the lattice parameters above \( T_{\text{OO}} \) cannot be fit to a \( T^1 \) or \( T \) power law, which is expected for the low-temperature (\( T \rightarrow 0 \)) or high-temperature (\( T \gg \theta_P \)) thermal expansion of an insulator, respectively [21]. Within a narrow temperature range, the data is fit to \( T^2 \) behavior [red lines in Figs. 4(a) and 4(b)]. Then the \( c \) lattice parameter around \( T_{\text{OO}} \) can be described as

\[
c(T) = c_0(1 + AT^2) + \Delta c. \tag{1}
\]

Here the spontaneous strain \( \Delta c \) is 0 above \( T_{\text{OO}} \), and below \( T_{\text{OO}} \) it is well represented by a single power-law form:

\[
\Delta c = B(1 - T/T_{\text{OO}})\beta, \quad \text{89 K} < T \leq T_c. \tag{2}
\]

The \( \Delta a \) could be fit in a similar fashion. Between 89 and 97 K (i.e., \( 1 - T/T_{\text{OO}} < 0.1 \)), the parameters obtained from the fitting using Eqs. (1) and (2) [insets of Figs. 4(a) and 4(b)] were \( T_{\text{OO}} = 97.0(2) \text{ K} \) and \( \beta = 0.35(2) \). The value for \( \beta \) is typical of orbital-ordering transitions, where it is interpreted as being a secondary order parameter that is quadratically coupled to the primary order parameter associated with the transition (i.e., the total exponent is twice as large as the expected 3D Heisenberg exponent of \( \beta = 0.35 \) [19]).

The first-principle calculation using combinations of the local-density approximation and the \( GW \) method [7] has predicted an orbital-ordering state in \( \text{Sr}_2\text{VO}_4 \) around 100 K with (i) the coexistence of the antiferromagnetism and ferromagnetism, (ii) a major percentage of orbitals along the \( c \) axis, (iii) a narrow Mott gap which suggests that this material is close to a metal-insulator transition. Our experimental results shown above are consistent with all these predictions. The orbital-ordering transition in \( \text{Sr}_2\text{VO}_4 \) confirms that the orbital degeneracy plays an important role in the layered perovskites. Future studies of the coupling of electronic effects to the lattice are essential toward developing a coherent picture of the differences among the layered cuprates, ruthenates, and vanadates.

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