Orbital fluctuations in the $S=\frac{1}{2}$ Mott insulator Sr_2VO_4

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We report a high-energy inelastic neutron-scattering study on Sr_2VO_4 that shows a transition from an orbital liquid phase at high temperature to an orbital-order phase at low temperature with an unquenched orbital angular momentum. Susceptibility under pressure shows a collapse of the magnetic phase transition due to enhanced orbital fluctuations. One possible explanation for our data is the recently proposed magnetically hidden order of Kramers doublets in d^1 electron systems.

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Layered perovskites provide a variety of examples of the complex behavior of strongly correlated electron systems; two celebrated cases are the high-temperature superconductor $La_{2-x}Sr_xCuO_4$ (Ref. 1) and the low-temperature superconductor Sr_2RuO_4.[2] Recently, another layered-perovskite Sr_2VO_4 has been investigated as a highly correlated system with strong orbital-ordering character. Sr_2VO_4 is isostructural to $La_{2-x}Sr_xCuO_4$ and Sr_2RuO_4, which have a K_2NiF_4 structure. The early studies[3–6] on Sr_2VO_4 show that the system is a Mott insulator in the whole temperature range with a magnetic transition temperature sensitive to the sample's quality. First-principles calculations on Sr_2VO_4 predict that a nontrivial orbital-stripe order emerges at $\sim$100 K for V^{4+} ($3d^1$) (Ref. 7) and Zhou *et al.*,[8] confirmed this prediction by magnetization and low-temperature x-ray diffraction measurements. The results showed a sudden enhancement of the c/a ratio below 110 K, that was initially interpreted as an orbital-ordering transition accompanied with an antiferromagnetic transition at $T_N \sim 110$ K.

Moreover, theoretical calculations predicted that Sr_2VO_4 could become a superconductor under uniaxial pressure along the c axis.[9] On the basis of these results, it seems plausible that the orbital-order phase competes with a superconducting phase to develop. Whether pressure will suppress the orbital-order phase and the related antiferromagnetic transition is not known. On the other hand, Jackeli and Khaliullin[10] recently suggested that a magnetically hidden order of Kramers doublets of d^1 electron induced by spin-orbital coupling is responsible for the phase transition in Sr_2VO_4. The model predicted an unconventional, magnetic octupolar ordering due to spin-orbit coupling, compatible with the tetragonal symmetry and characterized by a reduced magnetization, a strong magnetoelastic coupling and the absence of new Bragg peaks in a conventional neutron-scattering experiment. Despite the relevance of these theoretical predictions, there has been no experimental effort to date aimed to confirm the octupolar order in the low-temperature phase of Sr_2VO_4.

In this Brief Report, we report high-energy neutron-scattering and magnetic-susceptibility measurements under pressure in Sr_2VO_4. The neutron data reveals a transition from orbital liquid to orbital-ordering states with a tetragonal field ($\sim$105 meV). The pressure studies show a giant negative pressure dependence of the transition temperature, which indicates the existence of strong orbital fluctuations. One possible explanation for all these observations is the realization of a magnetically hidden order of Kramers doublets in Sr_2VO_4.

The sample Sr_2VO_4 was prepared by solid-state reaction.[8] The inelastic neutron-scattering experiments were carried out on powder samples using the high-energy transfer chopper spectrometer at the ISIS spallation neutron source with an incident energy of 200 and 2 meV resolution. The powder sample was cold pressed to form dense pellets and annealed again before being used for magnetic measurement. Pressures up to $P=10$ kbar were obtained in a Be-Cu cell from EASYLAB, using Sn as an internal manometer. The susceptibility measurements were done in a Quantum Design dc superconducting quantum interference device magnetometer with an applied magnetic field 0.2 T.

Figure 1 shows the high-energy neutron-scattering spectra with $T=4$, 200, 300, and 400 K. At 4 K, an excitation around 120 meV is observed, which is revealed to be two separate modes. With increasing temperature, this excitation becomes weak in intensity and the separation of the two modes decreases, although the excitation persists even at 400 K. The spectra integrated over $0.4<|Q|<5$ Å^{-1} at different temperatures are plotted in Fig. 2(a). At 4 K, the excitation around 120 meV could be fitted to two peaks [green lines in Fig. 2(a)], and the separation (ΔE) between them is 10.5 meV. With increasing temperature, these two peaks merge and ΔE is continuously reduced down to around 5 meV at 400 K. The temperature dependence of the integrated area of the peaks is shown in Fig. 2(b). The area begins to increase below 300 K, and saturates below 120 K, which indicates the excitation around 120 meV is related to the orbital-ordering transition. ΔE shows similar temperature dependence [Fig. 2(c)].

In Sr_2VO_4, the tetragonal crystal field (Δ_{CF}) due to the elongation of the c axis lifts the orbital degeneracy of the t_{2g}

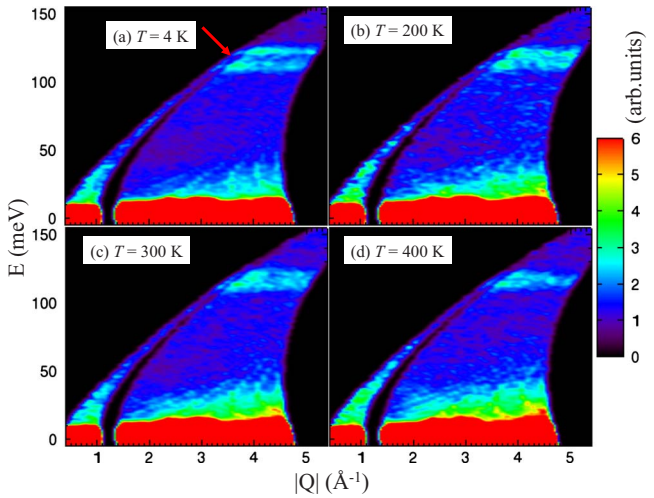

FIG. 1. (Color online) High-energy inelastic neutron-scattering spectra at (a) 4 K, (b) 200 K, (c) 300 K, and (d) 400 K for Sr_2VO_4. The red arrow in (a) shows the position of the excitations.

orbitals by pushing the d_{xy} orbital with an angular momentum $l_z=0$ to a higher energy. Until now, no experiments have directly determined the value of Δ_{CF}. By theoretical calculations, Imai *et al.*[7] suggested that $\Delta_{CF}\sim 80$ meV and Arita *et al.*[11] suggested $\Delta_{CF}\sim 125$ meV. Recently, Jackeli *et al.*[10] proposed that the orbital angular momentum of t_{2g} orbitals for Sr_2VO_4 is unquenched and the spin-orbital coupling (λ) is active. λ further splits d_{yz}/d_{xz} to two complex orbital states with angular momentum $l_z=\pm 1$ as $|l_z=\pm 1\rangle \equiv -\frac{1}{\sqrt{2}} \times (i|xz\rangle \pm |yz\rangle)$. Based on this scheme, Jackeli *et al.*[10] identified a magnetically ordered phase with a composite (spin plus orbital) order parameter in Sr_2VO_4. However, no static order is expected from this model for the spin and orbital moments, that remain only locally coupled. Hence, this phase will not show a conventional long-range order manifested in the emergence of Bragg peaks in a neutron-diffraction experiment.[3]

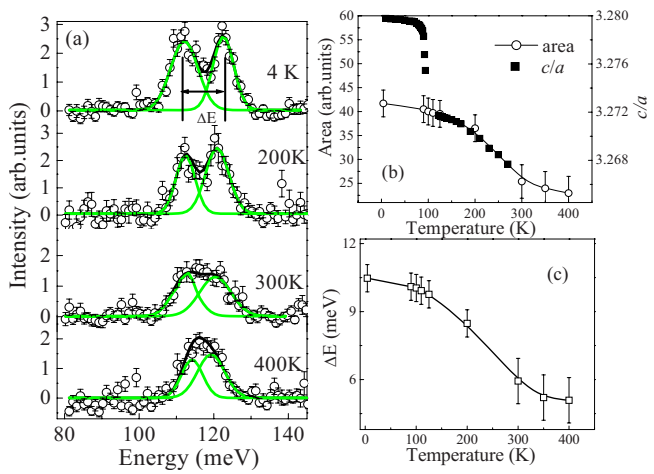

FIG. 2. (Color online) (a): the high-energy inelastic neutron scattering integrated over Q around 120 meV as a function of temperature; the green (light gray) lines are fittings to two peaks, the black line is the total fitting. (b) The temperature dependencies of the peaks' integrated area and c/a ratio (Ref. 8); (c) the temperature dependency of ΔE. The lines in (b) and (c) are guides to the eyes.

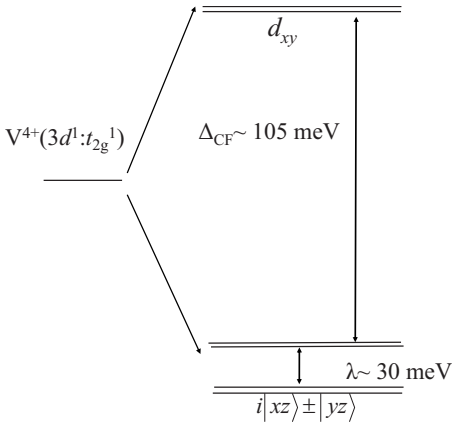

FIG. 3. The schematic t_{2g} orbital levels for V^{4+} ($3d^1$) electron: the t_{2g} level is split into three sets of Kramers doublets by a tetragonal crystal field Δ_{CF} and a spin-orbital coupling λ.

In fact, our observation of the excitation around 120 meV by neutron scattering is not trivial, and supports the existence of a complex orbital state with unquenched orbital angular momentum. Note that this transition would not couple to neutrons if the doublets are made of purely real orbitals such as d_{xz} or d_{yz} with quenched angular momentum. The very presence of finite intensity for neutron scattering is an important signature to support the existence of the complex spin-orbital local order of Kramers doublets. According to Jackeli *et al.*,[10] the largest spectral weight excitation is the nearly dispersionless interdoublet excitation at energy δ,

$$\delta = \lambda + 1/4[(2\Delta_{CF} - \lambda)(1/\cos(2\theta) + 1)], \quad (1)$$

where λ is the free-ion V^{4+} spin-orbital coupling, Δ_{CF} is the crystal-field splitting as indicated in Fig. 3, and θ is defined as[10]

$$\tan(2\theta) = 2\sqrt{2}\lambda/(\lambda - 2\Delta_{CF}). \quad (2)$$

With $\lambda=30$ meV for V^{4+} free ions, and $\Delta_{CF}=105$ meV, as shown in Fig. 3, the excitation energy δ is 120 meV. This energy scale correlates with recent estimates of the excitation gap to be close to 128 meV by Viennois *et al.*[12] (powder samples) and Matsuno *et al.*[6] (thin-film samples). Note that intradoublet excitations of lower energy and considerable dispersion have low spectral weight and are difficult to observe with neutron scattering. Single-crystal measurements are needed to see these modes.

As temperature increases, thermal fluctuations mix up the lowest two doublets increasing the orbital fluctuations between complex and real combinations of orbitals. As real d orbitals have quenched angular momentum, they do not contribute to the neutron scattering and hence the intensity (the integrated area) should go down, as observed [Fig. 2(b)]. The temperature dependence of the integrated area is very similar to that of the c/a ratio, as shown in Fig. 2(b), which is a measure of the strain related to the orbital-ordering or orbital fluctuations.[13] It is worth noting that the intensity of the excitations shows no jump around the transition as the c/a ratio does. One possible reason is that this is a very small effect that we cannot probe accurately to within the resolution of

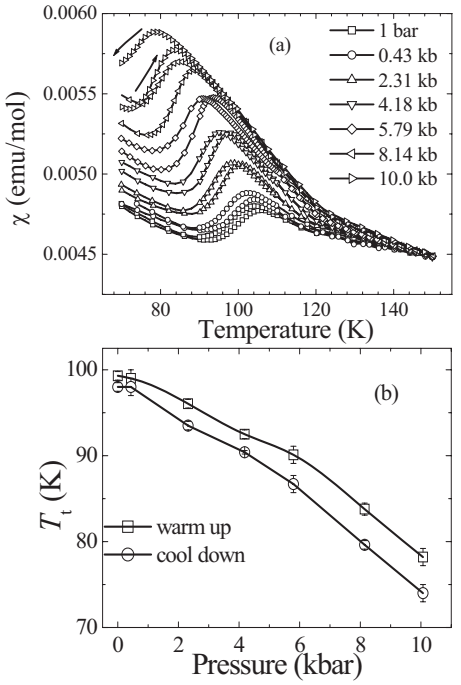

FIG. 4. (a) Temperature dependencies of the susceptibility of Sr_2VO_4 at different pressures and the arrows represent the warming up run and cooling down run. (b) Pressure dependencies of T_t, the lines are guides to the eyes.

the instrument. For example, due to the relatively high-energy scale for the excitation -120 meV ~ 1300 K, even at 400 K there should not be much of an intensity change. There is also the issue of phase separation which complicates a direct interpretation of the intensity of the modes near the phase transition. The splitting of the excitations as a function of temperature can now be understood as a Zeeman-type splitting of the doublets as the ordered phase is approached from high temperatures. This splitting correlates with the increased orbital fluctuations and the decrease in the c/a ratio. This again shows that the weak excitations at high temperature are associated with orbital fluctuations in a precursor orbital liquidlike phase.

In order to further confirm the nature of the low-temperature phase, we have studied the temperature dependence of the magnetic susceptibility under pressure. At ambient pressure the susceptibility shows an abrupt transition toward a low-temperature state of reduced magnetization at $T_t=99.5$ K (defined as the inflection point of the susceptibility). A thermal hysteresis between the warming up and cooling down runs of about 1.3 K is observed, which is consistent with a first-order character of the phase transition. Increasing pressure results in a rapid decrease in T_t of about 20 K in $P=10$ kbar, as shown in Fig. 4. Increasing pressure also results in an increase in the magnetization in the low-temperature phase.

In a Mott insulator, the superexchange interaction between the Kramers doublets can induce a magnetically ordered phase below T_N that lifts the degeneracy and breaks time-reversal symmetry. The value of the exchange interaction is determined by the ratio between the spin-dependent expectation value for the charge transfer between sites, t, and the Coulomb repulsion term, U, as $J \propto t^2/U$.[14] Given the dependence of t on the interatomic distance through the overlap integral[15] and assuming a pressure-independent U, T_N increases with pressure at a given rate. This is the basis of the Bloch's rule[16] $[\alpha_B \equiv (d \ln T_N/dP)/(d \ln V/dP) \approx -3.3]$, obeyed by the vast majority of magnetic insulators. The magnitude of $d \ln T_N/dP$ falls into a range $2.1\times10^{-3}-2.5\times10^{-3}$ $(\text{kbar})^{-1}$ for ionic magnetic insulators.[17,18] However, this is opposite to what we observed in Sr_2VO_4, where T_t decreases with pressure at a approximate rate of $d \ln T_t/dP = -23.0\times10^{-3}$ $(\text{kbar})^{-1}$. The dramatic negative pressure dependence of T_t observed in Sr_2VO_4 shows that simple mean-field superexchange theory is not applicable to this system. Instead, the collapse of T_t is naturally explained by the existence of an ordered phase of spin-orbital objects of the type described by Jackeli and Khaliullin.[10] The first-order phase transition occurs in this scenario by the interplay between interdoublet and intradoublet excitations, which correlates very well with the report of an abrupt change in the c/a lattice parameters at T_t. On the other hand, the nonmagnetic nature of the doublet agrees with the drop in the magnetic susceptibility. Increasing pressure decreases the splitting between the two lowest doublets and hence increases orbital fluctuations. Although the superexchange increases with increasing pressure, ordering of spins/orbitals is suppressed (contrary to naive expectation), because orbital fluctuations are highly detrimental for ordering.[19]

In many other orbital-ordering systems, orbital fluctuations also have been confirmed to occur at high temperatures. For example, in the orbital-ordering systems with orthorhombic structure, $LaTiO_3$ with Ti^{4+} $(3d^1)$ (Ref. 20) and YVO_3 with V^{3+} $(3d^2)$,[21] the orbital fluctuations sufficiently suppress the phonons and lead to a glassylike thermal conductivity at high temperatures above the orbital-ordering transition. The inelastic neutron scattering of YVO_3 also reveals dynamic orbital states at high temperatures.[22] The theoretical studies also support an orbital liquid phase in $LaTiO_3$ (Refs. 23 and 24) and orbital fluctuations in YVO_3.[19,22] However, in $LaTiO_3$ (Ref. 25) and YVO_3,[26] the orbital-ordering transition temperatures increase with increasing pressure, which indicates the mean-field exchange interaction still dominates the spin/orbital ordering despite the existence of orbital fluctuations in these orthorhombic systems. Sr_2VO_4 is an unique system in which the effect from enhanced orbital fluctuations overcomes the effect of the mean-field exchange interactions to lead a collapse of ordering under pressure. Sr_2VO_4 has an ideal tetragonality and thus orbital moments can perfectly survive, which gives a way to realize the magnetically hidden order of Kramers doublets where spin and orbital moments compensate and the order parameter has octupolar symmetry. As discussed above, the occupation of complex orbitals could be the reason for the abnormal enhanced orbital fluctuations in Sr_2VO_4.

In summary, we have identified two distinct phases in Sr_2VO_4: (i) an orbital liquid at high temperatures where orbital fluctuations are strong. In this liquid state, the lowest

two orbital doublets are mixed up due to the superexchange interactions. Orbitals are neither pure complex nor pure real due to the effect of thermal fluctuations. (ii) An orbital-order phase at low temperatures in which the ground-state orbitals are complex and have unquenched angular momentum. The ordering temperature for the orbital liquid to orbital-order phase transition is significantly suppressed by increasing pressure due to the enhanced orbital fluctuations between the lowest two doublets. One possible explanation for the characteristics of this low-temperature phase is a local order of Kramers doublets in a d^1 system due to spin-orbital coupling. The neutron measurements show that the t_{2g} orbitals are split by a $\Delta_{CF} \simeq 105$ meV, which also is consistent with the theoretical calculations.

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