Anomalous metallic state in the vicinity of Metal to Valence Bond Solid insulator transition in LiVS₂

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We investigate LiVS₂ and LiVSe₂ with a triangular lattice as itinerant analogues of LiVO₂, known for the formation of valence bond solid (VBS) state out of S = 1 frustrated magnet. LiVS₂, which is located at the border between a metal and a correlated insulator, shows a first ordered transition from a paramagnetic metal to a VBS insulator at Tc ~ 305 K upon cooling. The presence of VBS state in the close vicinity of insulator-metal transition may suggest the importance of itinerancy in the formation of VBS state. We argue that the high temperature metallic phase of LiVS₂ has a pseudo-gap, likely originating from the VBS fluctuation. LiVSe₂ was found to be a paramagnetic metal down to 2 K.

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Transition metal compounds with a geometrically frustrated lattice, such as a triangular and a pyrochlore lattice, often form a valence bond solid (VBS) state at low temperatures. When the t₂g orbitals are partially occupied, utilizing orbital degrees of freedom, complex “molecular” clusters in a spin singlet state are often formed: trimer in LiVO₂, heptamer in AlV₂O₄, helical dimer in MgTi₂O₄ and octamer in CuIr₂S₄. A VBS state was found also in organic systems with geometrical frustration. Very recently, Shimizu et al. demonstrated that the VBS state can be melted by applying hydrostatic pressure P on the organic compound EtMe₃P[Pd(dmit)₂] with a triangular lattice. Remarkably, superconductivity appears as soon as the VBS state is suppressed by P.

A question that arises is whether or not similar melting of the VBS state and appearance of exotic metallic phases can occur in inorganic frustrated systems. In the inorganic systems, however, application of an external pressure is expected not to melt but to stabilize VBS due to a predominant volume effect. In CuIr₂S₄, the lattice shrinks appreciably in the VBS phase due to the formation of strongly bonded singlet molecules in the VBS and the pressure can be stabilized through -pV (p : pressure, V : volume) term in the corresponding free energy. Effects of negative pressure on the VBS states of inorganic systems, on the other hand, have not been investigated so far.

The inorganic LiVO₂ in which the magnetic V³⁺ ions (3d², S = 1) form a triangular lattice is known to be a paramagnetic insulator with strong antiferromagnetic interactions between the localized S = 1 moments at high temperatures. Upon cooling, at Tc ~ 500 K, LiVO₂ exhibits a first ordered phase transition to a VBS state with a characteristic spin gap of ~ 1600 K, evidenced by the formation of vanadium trimers. With this system, one can apply “negative” pressure by replacing oxygens with larger anions such as S and Se. More over, the negative pressure may increase the overlap between V 3d and p-orbital (O 2p, S 3p, and Se 4p), and increase the electronic band width. Thus, this vanadium-based triangular system provides a good opportunity to study effects of negative pressure on VBS states in inorganic materials.

In this Letter, we demonstrate that LiVS₂ is indeed an itinerant analogue of LiVO₂ with suppressed VBS. We found that in LiVS₂ a phase transition from a paramagnetic metal to a trimer VBS insulator occurs at Tc ~ 305 K that is lower than that of LiVO₂. In LiVSe₂ with highest negative pressure, the phase transition is suppressed down to 2 K. In the high temperature metallic phase of LiVS₂, strong temperature dependence of the bulk susceptibility, χ, was observed, which is similar to the pseudo-gap behavior found in underdoped superconducting cuprates. We argue this is an evidence for a pseudo-gap formation by short-range spin singlet fluctuations in the paramagnetic metallic phase of LiVS₂.

Powder samples of LiVS₂, LiVSe₂ and their solid solution LiVS₂-xSeₓ were prepared by a soft-chemical method followed by a solid-state reaction. For LiVS₂-xSeₓ (0 ≤ x ≤ 0.4), Li-deficient Liₐ₋₀.₇₅VS₂₋ₓSeₓ was obtained first, by a reaction of an appropriate amount of Li₂S, V, S and Se in an evacuated quartz tube at 700 °C for 3 days. For LiVSe₂, VSe₂ was synthesized from an appropriate amount of V and Se at the same condition with Li₋₀.₇₅VS₂₋ₓSeₓ. The products were immersed in 0.2 M n-BuLi hexane solution for 4
FIG. 1: (Color online) Schematic phase diagram in LiVO$_2$, LiVS$_2$ and LiVSe$_2$ system. Spin pseudo-gap is observed in the white region in the metallic phase. The left inset shows schematic VBS state on the triangular lattice of V$^{3+}$. The red circles denote the V ions. The right inset shows the phase diagram in the vicinity of the VBS transition. Filled circles denote the VBS transition obtained from magnetic measurements for the solid solution LiVS$_{2-x}$Se$_x$.

LiVS$_2$ exhibits a first ordered metal to insulator transition at $T_c \sim 305$ K, shown in Fig.2. At high temperatures above $T_c$, the resistivity is about 40 m$\Omega$cm and almost temperature independent. Since the sample is low temperature sintered polycrystal, empirically, the intrinsic resistivity can be more than 1 order of magnitude smaller than 40 m$\Omega$cm, consistent with the metallic nature. Accompanied with the metal to insulator transition, an abrupt decrease in the magnetic susceptibility is observed, as shown in Fig.2. The system is very likely to be nonmagnetic below $T_c$ with a temperature-independent Van Vleck term and a tiny low-temperature Curie tail, which corresponds to paramagnetic impurities of $\sim 1\%$ if we assume spin 1/2 moment. In accord with the nonmagnetic behavior of LiVS$_2$, $^{51}$V NMR relaxation rate $T_1^{-1}$ shows thermally activated behavior, from which we estimate a spin gap of $\Delta = 1900$ K [17].

Despite the metallic behaviors above $T_c$, electron diffraction measurements on LiVS$_2$ show an evidence for the formation of the V trimers below $T_c$ which indicates development of the same VBS state as in the insulating LiVO$_2$. The electron diffraction pattern reveals sharp superlattice reflections at $\{1/3 1/3 0\}$ below $T_c \sim 305$ K, as in Fig.3. The superlattice reflections correspond to a $\sqrt{3}a \times \sqrt{3}a$ superlattice in real space, suggesting a formation of vanadium trimers in the VS$_2$ plane, shown in the right inset of Fig.3. The Fourier-transformed patterns of EXAFS spectra, shown in Fig.3, is indeed consistent with the vanadium trimers in low temperature phase. Below $T_c$, spectra shows clear three peaks between 1.5 and 3.5
FIG. 3: (Color online) Fourier transforms of the EXAFS spectra of LiVS$_2$ at 20 K. The lower right inset shows vanadium trimer schematically. The V-V distances and the displacement of the V from the regular triangular lattice, $\delta$, are determined from the data taken at 200 K. The upper panels show the electron diffraction pattern along the [001] zone axis of LiVS$_2$.

Å. The first peak at around 2 Å is ascribed to that from the first-neighbor V-S. The second and third peaks, marked by arrows, are ascribed to those from the first-neighbor V-V bonds, indicating the presence of two inequivalent V bonds as expected for V trimer formation. Note the large splitting of more than 10 %, indicative of a local character of V trimer.

Associated with the formation of VBS state with V trimers, the volume contraction originates from the large in-plane contraction. We observed the volume contraction of $\sim 0.3$ % as shown in Fig.4, which is a factor of two smaller than that of LiVO$_2$ [11]. The DSC measurement shown in Fig.4 indicates the increase of entropy $\Delta S \sim 6.4$ J/mol K at the VBS transition. This should give rise to a positive pressure coefficient of VBS transition temperature $dT_c/dP = \Delta V/\Delta S \sim 20$ K/GPa from Clausius-Clapeyron relationship. Indeed, we observe an increase of $T_c$ under an external pressure of a comparable magnitude in Fig.4, which implies the pressure induced stabilization of VBS simply reflects the volume contraction and the low entropy in the VBS phase.

The high temperature metallic phase above $T_c \sim 305$ K in LiVS$_2$, namely realized at the close vicinity to VBS, is not a simple metal but a pseudo-gap metal. The magnetic susceptibility in this high temperature metallic phase is $\sim 5 \times 10^{-4}$ emu/mol, which yields an estimate of electronic specific heat gamma $\gamma \sim 35$ mJ/mol K$^2$, assuming the Wilson Ration $R_W \sim 1$. Since $R_W$ in correlated metals are normally 1.5-2.0, a better estimate for gamma may be $\gamma \sim 20$ mJ/mol K$^2$. This is indeed consistent with the entropy change $\Delta S \sim 6.4$ J/mol K at the VBS transition. $\Delta S$ for LiVS$_2$ is smaller than that for its insulating analogue LiVO$_2$ ($\Delta S \sim 14.5$ J/mol K [18]), indicating that high temperature metallic state of LiVS$_2$ has lower entropy than the high temperature phase of LiVO$_2$, which may be reasonably ascribed to a Fermi degeneracy in the metallic phase. Considering that $\Delta S$ for LiVO$_2$ is only roughly twice of $\Delta S$ for LiVS$_2$, LiVS$_2$ may locate close to LiVO$_2$ in the phase diagram, shown in Fig.1. Assuming the observed $\Delta S$ in LiVS$_2$ originates from the electronic gamma $\gamma \sim 21$ mJ/mol K$^2$, which is in good agreement with the estimate from the magnetic susceptibility. These point that LiVS$_2$ at high temperatures is a paramagnetic metal with a moderate density of states at the Fermi level, comparable to those of other

FIG. 4: (Color online) The upper panel shows temperature dependence of lattice parameters $a$, $c$ and unit cell volume $v$. The middle panel shows differential scanning calorimetry (DSC) signals of LiVS$_2$. The lower panel shows magnetic susceptibility data of LiVS$_2$ under hydrostatic pressure. The measurements of lattice parameters and magnetic susceptibility were performed on cooling process, while DSC measurements were performed on both cooling and heating processes as indicated by arrows.
same behavior of susceptibility was observed for powder under-doped high-$T_c$ cuprates with pseudo-gap. The same behavior of susceptibility was observed for powder sample previously \[10\]. By replacing S with Se in LiVS$_2$, we can suppress the VBS and increase the band width further. As shown in Fig.2, we indeed find that LiVSe$_2$ is a paramagnetic metal down to 2 K without any trace of anomalous decrease of susceptibility, implying that the magnetic susceptibility shows a rapid decrease on cooling temperature, which is reminiscent of those of under-doped high-$T_c$ cuprates with pseudo-gap. The systematic evolution of electronic states on going from O, S to Se is clear and can be summarized by a schematic phase shown in Fig.1. Note the increased magnitude of susceptibility in LiVSe$_2$ compared with LiVS$_2$ despite the increased band width. This implies that the density of states of LiVS$_2$ is suppressed by some mechanism, which we take evidence of pseudo-gap. In the electron diffraction pattern of LiVS$_2$, we indeed find that LiVSe$_2$ is a paramagnetic metal to valence bond solid (VBS) insulator transition. The systematic evolution of electronic states on going from O, S to Se is clear and can be summarized by a schematic phase shown in Fig.1. Note the increased magnitude of susceptibility in LiVSe$_2$ compared with LiVS$_2$ despite the increased band width. This implies that the density of states of LiVS$_2$ is suppressed by some mechanism, which we take evidence of pseudo-gap. The electron diffraction pattern of LiVS$_2$ in the high temperature phase (Fig.3), we observe a diffuse scattering indicative of short-range (and dynamic) trimer formation. This leads us to speculate that the origin of pseudo-gap in the metallic LiVS$_2$ is a singlet fluctuation.

As summarized in Fig.1, VBS state robustly appears from the insulating side to the metallic side. VBS eventually vanishes for LiVSe$_2$ perhaps due to a combined effect of the increased band width and the lattice expansion. VBS formation in LiVO$_2$ had been discussed in terms of novel interplay of spin and orbital degrees of freedom in geometrically frustrated magnet \[21\]. The presence of VBS over the metal-insulator crossover region suggests that, in contrast to the conventional picture, electron transfer (itinerancy) might play a central role in realizing the VBS, as in the orbitally driven Peierls transition in CuIr$_2$S$_4$ and MgTi$_2$O$_4$ \[21\].

Very recently, T. Itou et al. demonstrated the absence of pseudo-gap in the superconducting EMe$_3$P[Pd(dmit)$_2$]$_2$ by NMR measurement \[22\], indicating that the pseudo-gap metallic state is unique to the present LiVX$_2$ system. It may be interesting to further suppress VBS from LiVS$_2$ to $T = 0$ with substitution of S with Se and to explore the exotic metal formed near possible VBS critical point. In the LiVS$_2$–Se$_x$ solid solution, we indeed observed a systematic decrease of magnetic susceptibility anomaly representing the VBS transition upon Se substitution and a disappearance around $x = 0.3$, shown in the right inset of Fig.1. We found, however, that all the Se substituted samples show a weakly insulating behavior, perhaps due to the disorder effect inherent to the Se substitution, and the exotic metal phase including superconductivity could not have been explored.

In conclusion, we have identified a crossover from $S = 1$ Mott insulator to a paramagnetic metal in a series of triangular lattice vanadates, LiVX$_2$ with $X = O$, S and Se. LiVS$_2$ is located at the crossover region and a paramagnetic metal to valence bond solid (VBS) insulator transition was observed as a function of temperature. We argue the high temperature metallic phase in LiVS$_2$ is a pseudo-gap metal with possible spin singlet correlation, due to the close proximity to the VBS state, which provides a new playground for the novel interplay of strong electron correlation and the geometrical frustration.

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