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# Enhanced Pressure Dependence of Magnetic Exchange in $A^{2+}[V_2]O_4$ Spinels Approaching the Itinerant Electron Limit

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We report a systematic enhancement of the pressure dependence of $T_N$ in $A^{2+}[V_2]O_4$ spinels as the V-V separation approaches the critical separation for a transition to itinerant-electron behavior. An intermediate phase between localized and itinerant-electron behavior is identified in $Zn[V_2]O_4$ and $Mg[V_2]O_4$ exhibiting mobile holes as large polarons. Partial electronic delocalization, cooperative ordering of V-V pairs in $Zn[V_2]O_4$ below $T_s \approx T_N$ and $dT_N/dP < 0$, signals that lattice instabilities associated with the electronic crossover are a universal phenomenon.

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Paramagnetic metals and Mott-Hubbard insulators represent two fundamentally different phases that can be interchanged by increasing or decreasing electronic correlations through a first-order quantum phase transition (QPT) [1].

On approaching the QPT from the itinerant-electron side, a strong renormalization of the effective mass and the Pauli susceptibility of the metal is expected, diverging at a critical value of the interaction strength ($U = U_C$ at the QPT) [2]. The correct description of the electronic properties at this point, where neither crystal-field nor band theory are fully applicable, remains a challenge.

The same fundamental problem is found on approaching the QPT from the localized limit. In this case the rapid increase of the spin-dependent expectation value for the charge transfer between sites, $t$, against the intra-atomic Coulomb energy, $U$, is expected to invalidate the spin-spin superexchange interaction formula [3,4]

$$J \propto \frac{t^2}{U}. \tag{1}$$

Since $t$ is proportional to the overlap integral for the donor and acceptor orbitals on neighboring atoms, $t$ is also a function of the interionic distance, $R$. This volume dependence has been calculated by Harrison [5] for direct exchange between $d$ orbitals to be $J \propto V^{-10/3}$, which is the basis of the phenomenological Bloch's equation [6] for magnetic insulators: $\alpha = (\partial \ln T_N / \partial \ln V) \approx -3.3$ provided $U$ remains constant. This behavior is so general that small deviations from the predicted value of $\alpha$ have been used to define the limit of applicability of crystal-field theory when approaching the itinerant-electron behavior [7,8].

In this Letter, by using Bloch's criterion to monitor the approach to the QPT, we report the observation of an anomalous and systematic increase in Bloch's parameter $\alpha$ as the metal-metal distance is reduced along the $A^{2+}V_2O_4$ series. Our results suggest that the passage from the localized to the itinerant-electron limit occurs through an intermediate phase, in which electronic delocalization in cation clusters (molecular orbitals) occurs in an ionic matrix. This supports the universality of the first-order character of the transition and the stabilization of an intermediate phase in which there is a disproportionation into molecular orbitals within clusters and weak bonding between clusters [9,10].

Single-phase, polycrystalline $A[V_2]O_4$ spinels were synthesized by solid-state reaction in evacuated quartz ampoules. Structural parameters were derived from x-ray diffraction patterns by Rietveld analysis. Magnetic measurements under pressure up to $P = 10$ kbar were obtained in a Be-Cu cell. Lattice compressibility was measured by fitting the pressure dependence of the lattice volume (up to 50 kbar) with the Birch-Murnaghan equation. *Ab initio* density-functional-theory (DFT) calculations were performed within a full-potential, all-electron approximation with the WIEN2K software [11]. Strong correlations were modeled by means of a hybrid DFT scheme for correlated electrons, the Perdew-Burke-Ernzerhol (PBE) + exact exchange functional [12].

The octahedral-site ions of a spinel form a pyrochlore lattice, which is geometrically frustrated for antiferromagnetic interactions. Consequently, $T_N$ is reduced considerably from the value expected on the basis of the Weiss constant $\theta_W$ of the Curie-Weiss paramagnetic susceptibility, and an enormous $\theta_W/T_N$ ratio results [13]. However, the geometric frustration remains volume-independent provided the lattice symmetry is not changed by the pressure. Therefore, Bloch's rule, $\alpha \approx 3.3$, should remain applicable to spinels where octahedral-site interactions are dominant. In order to test this conclusion, we measured $\alpha$

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for the $A[Cr_2]O_4$ spinels since they have a Cr-Cr distance much larger than the critical distance for metallic behavior, $R_c \approx 2.84$ Å [14]. In order to maximize $R > R_c$, we have chosen to measure $\alpha$ for $Mn[Cr_2]O_4$ having $R = 2.93(1)$ Å. In this spinel, given the electronic configuration of $Cr^{3+}$, the Cr-Cr interactions should dominate over the Mn-O-Cr interactions [15]. By fitting total energy calculations to a Heisenberg model, we calculated a $J_{\text{Cr-Cr}}/J_{\text{Cr-Mn}} \approx 3$, confirming this hypothesis.

Magnetization curves of $Mn[Cr_2]O_4$ measured around $T_N$ for different pressures are shown in Fig. 1. The finite magnetization below $T_N$ is due to the formation of a complex spiral-spin configuration in this frustrated ferrimagnet [16]. The data of Fig. 1 give a $T_N^{-1} dT_N/dP = 1.7 \times 10^{-3}$ kbar$^{-1}$; with a measured compressibility $\kappa = 4.95 \times 10^{-4}$ kbar$^{-1}$, $\alpha = 3.4(1)$ is obtained for $Mn[Cr_2]O_4$. This value follows nicely the Bloch rule for the Cr-Cr interactions, which validates our use of $\alpha$ as an indicator whether any of the $A[Cr_2]O_4$ spinels approach the transition to itinerant-electron behavior from the localized side.

Figure 2 shows the evolution of $T_N$ with the inverse V-V separation, $1/R_{\text{V-V}}$, for the $A[V_2]O_4$ spinels. Such an evolution has been predicted for the approach to metallic behavior from the localized-electron side [17]. As the overlap integral in $t$ of Eq. (1) increases with decreasing $R_{\text{V-V}}$, the energy $U$ must decrease or remain constant. Therefore, within the localized-electron superexchange represented by Eq. (1), $T_N$ should increase with decreasing V-V separation, i.e., increasing $1/R_{\text{V-V}}$. Therefore, we assign $Cd[V_2]O_4$ and $Mn[V_2]O_4$ to a localized-electron regime, Phase I. The spinels $Zn[V_2]O_4$ and $Mg[V_2]O_4$, which fall in the shaded region of Fig. 2, we assign to a Phase II intermediate between Phase I and an itinerant-electron Phase III. Rogers *et al.* [18] found that the activation energy $\Delta E$ for the resistivity decreased progressively as $R_{\text{V-V}}$ decreases. Our own measurements indicate that $\Delta E$ for $Mg[V_2]O_4$ is 3 times smaller than for $Cd[V_2]O_4$.

Although $A$-site $Mn^{2+}$ has a magnetic moment, the inclusion of $Mn[V_2]O_4$ in Fig. 2 is fully justified. The $t^2e^0$ configuration of a $V^{3+}$ ion allows for a V-V interaction across the shared octahedral-site edges that is strong relative to the Mn-O-V interactions [19] as in $Mn[Cr_2]O_4$. Our *ab initio* calculations fit to a Heisenberg model ($H = -\Sigma_{ij} J_{ij} S_i S_j$), as we did for $Mn[Cr_2]O_4$, yielded $J_{\text{V-V}} = +20$ K, $J_{\text{Mn-V}} = -9$ K, and $J_{\text{Mn-Mn}} = -0.3$ K, this latter value agreeing with that found experimentally for $Mn[Al_2]O_4$ [20].

Given the applicability of Bloch's rule to spinels with a dominant superexchange interaction between octahedral-site ions, we now demonstrate the progressive increase of $\alpha$ from the Bloch value of 3.3 as the V-V separation decreases in the $A[V_2]O_4$ spinels. Figure 3 shows the pressure dependence of $T_N$ for $Cd[V_2]O_4$ and $Mn[V_2]O_4$; the data give a $T_N^{-1} dT_N/dP = 2.7(4) \times 10^{-3}$ kbar$^{-1}$ for $Cd[V_2]O_4$ and an anomalously large $5.6(3) \times 10^{-3}$ kbar$^{-1}$ for $Mn[V_2]O_4$. We have measured a compressibility $\kappa = 5.88 \times 10^{-4}$ kbar$^{-1}$ for $Mn[V_2]O_4$, a little larger than the $\kappa = 4.95 \times 10^{-4}$ kbar$^{-1}$ obtained for $Mn[Cr_2]O_4$. Given a compressibility $\kappa = 6.6 \times 10^{-4}$ kbar$^{-1}$ for $Cd[V_2]O_4$ [21], we obtain the Bloch parameters $\alpha \approx 4.1(1)$ for $Cd[V_2]O_4$ and $\alpha \approx 9.9(1)$ for $Mn[V_2]O_4$. The value of $T_N^{-1} dT_N/dP$ for $Mn[V_2]O_4$ was obtained with two different measurements, giving the same $\alpha$, the largest reported so far in an oxide. This large value of $\alpha$ reflects an anomalous compressibility near $T_N$ as predicated for a double-well potential at the crossover from a longer to a shorter equilibrium V-V bond. Moreover, these results signal that the assumption of a pressure-independent energy $U$ in the localized-electron superexchange theory behind Eq. (1) is breaking down at the transition from Phase I to Phase II of Fig. 2.

Probably, the most relevant consequence of this study is that, in the transitional Phase II, neither the localized-electron nor the itinerant-electron model is applicable; the $V^{3+}$-$3d$ electrons are in a state that, at low tempera-

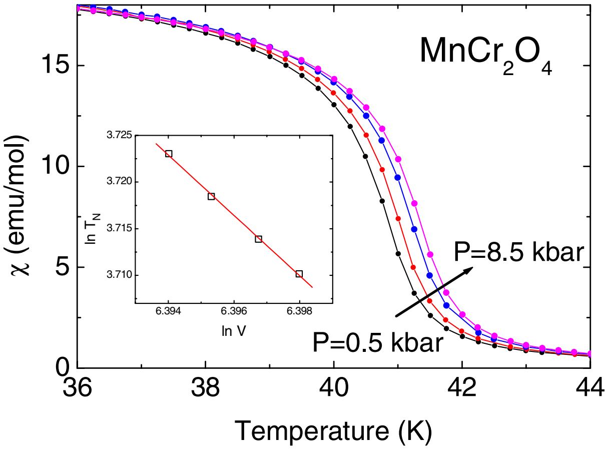

FIG. 1 (color online). Pressure and temperature dependence of the magnetization ($H = 100$ Oe) around $T_N$ in $Mn[Cr_2]O_4$. Inset: Fit of the experimental data to Bloch's equation (see the text).

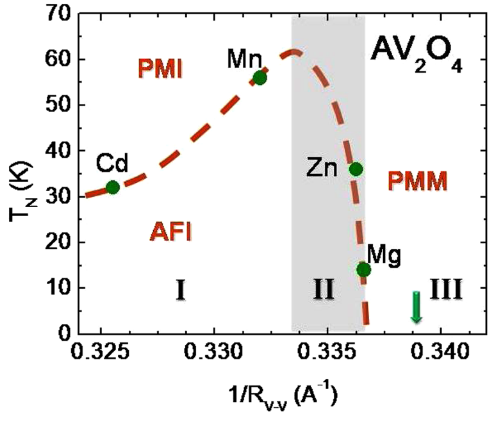

FIG. 2 (color online). Magnetic phase diagram of $A[V_2]O_4$ spinels as a function of the V-V distance. The dotted line is a guide to the eye. The vertical arrow marks the estimated critical distance for itinerant-electron behavior (Ref. [14]).

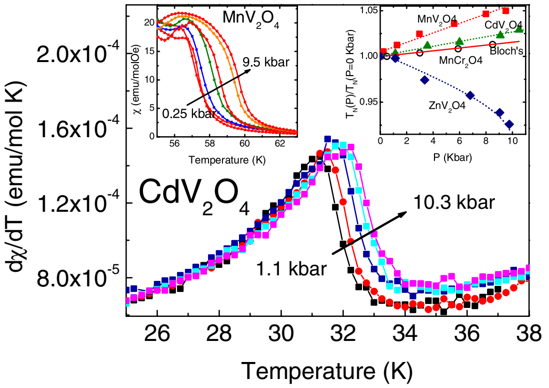

FIG. 3 (color online). Pressure dependence of $T_N$ in Cd[V$_2$]O$_4$. We represent the derivative of $\chi(T)$, in order to determine $T_N(P)$ accurately. Left inset: $\chi(T)$ for Mn[V$_2$]O$_4$ at different pressures around $T_N$. Right inset: evolution of $T_N$ for the samples of this work. The solid line represents $T_N(P)$ estimated from Bloch's law, with $\kappa = 5 \times 10^{-4}$ kbar$^{-1}$, appropriate for the cubic spinels.

tures, approaches a QPT from the localized-electron side. If the transition from localized to itinerant electronic behavior is first order, a bond disproportionation into molecular orbitals within cation clusters and weak bonding between clusters can be anticipated as occurs in LiVO$_2$. Moreover, any mobile charge carriers present due to nonstoichiometry can be expected to change from small polarons dressed in a local site distortion to carriers occupying larger cation clusters. Large polarons are distinguishable from small polarons in a measurement of the thermoelectric power.

The temperature dependence of the thermoelectric power, $S(T)$, is shown in Fig. 4 for the $A$[V$_2$]O$_4$ spinels. The large value of $S(T)$ shows that there is only a low density of mobile holes in these nearly stoichiometric oxides. Thermally activated behavior, typical of the trapping of small polarons at the defects that created them, is observed for Cd[V$_2$]O$_4$ and Mn[V$_2$]O$_4$. Note that although the Seebeck coefficient and the activation energy for the resistivity are very similar for Cd and Mn systems (they are both strongly localized), their values of $\alpha$ differ considerably (see Fig. 3). This is an indication of the extreme sensitivity of $\alpha$ to any change in the $U/t$ ratio close to a QPT.

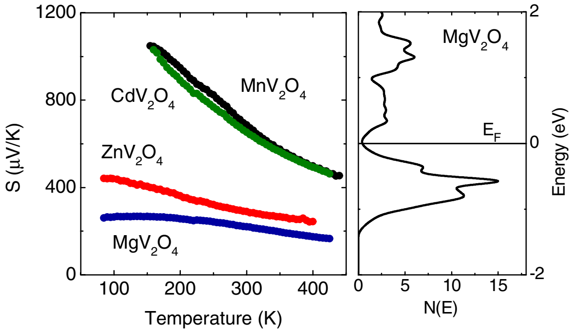

FIG. 4 (color online). Thermoelectric power of the series $A$[V$_2$]O$_4$. Reduction in the absolute value and loss of typical activated behavior is evident in Zn and Mg samples, both in the shadowed area of the phase diagram in Fig. 2. Right panel: calculated total density of states for MgV$_2$O$_4$ at $P = 8$ GPa. At this pressure, $R_{\text{V-V}}$ is predicted $\approx 2.931$ Å ($< R_C$) and the system to be metallic.

Zn[V$_2$]O$_4$ and Mg[V$_2$]O$_4$, on the other hand, exhibit a considerably reduced activation energy that, in the case of Mg[V$_2$]O$_4$, shows a nonactivated hole conduction at lowest temperatures that is reminiscent of the behavior of the minority-spin charge carriers of Fe$_3$O$_4$ between the Verwey transition (≈120 K) and room temperature [22].

Consistent with this indication that Zn[V$_2$]O$_4$ and Mg[V$_2$]O$_4$ belong to a transitional phase is the observation in both spinels of a first-order low-temperature tetragonal ($c/a < 1$) to a high-temperature cubic transition at $T_s$. These transitions are characteristic of a cooperative ordering of strong V-V bonding at the expense of weak V-V bonds as itinerant-electron behavior is approached from the localized-electron side. Although the driving force for these phase transitions is still under discussion [23–26], our results show a $U \gg t$ starting point could be appropriate for systems in region I, but not for those on region II of the phase diagram. With an angle $\alpha = 60°$ between nearest V-V bonds for the $yz$ and $zx$ orbitals, the tetragonal distortion may be characterized by a Peierls dimer formation in 1D chains along [011] and [101] directions. The situation is analogous to the formation of V$_3$ trimers within the VO$_2$ planes of LiVO$_2$. Cooperative ordering of metal-metal bonds is a common phenomenon at the crossover from localized to itinerant electronic behavior as is illustrated by the spinels Cu[Ir$_2$]S$_4$ and Mg[Ti$_2$]O$_4$ [27,28] as well as by numerous molybdates [9].

Experimental NMR, muon spin resonance, and neutron-diffraction or neutron-scattering studies [29–31] have demonstrated that, if present, the V-V pairing in the tetragonal phase does not suppress totally the spin on a vanadium ion nor remove geometric frustration completely, leading to a short-range magnetic order below $T_N \approx T_S$ and an incommensurate spin-density wave. This finding may be characteristic of homopolar bonding where the metal-metal separation remains $R \geq R_C$. Figure 5 shows the effect of pressure on the magnetic susceptibility of Zn[V$_2$]O$_4$. At ambient pressure, the susceptibility drops sharply on cooling through $T_s = 38$ K due to the spin pairing in the V-V bonds (see $\chi$ and C$_p$ in the inset of Fig. 5). Under pressure, the two-peak structure of the plot of $d\chi/dT$ vs $T$ associated with $T_s$ and $T_N$ is resolved. Given $c/a < 1$ in the tetragonal phase, the peak that decreases its temperature with pressure is ascribed to $T_N$. If the residual spins on the V-V pairs are reduced by pressure, the long-range magnetic ordering temperature $T_N$ is reduced. Long-range magnetic order and any V$^{3+}$-ion spin may be completely suppressed below $T_s$ in Mg[V$_2$]O$_4$.

Finally, given the experimental compressibility of $5.88 \times 10^{-7}$ bar$^{-1}$ and $R_C \approx 2.94$ Å (see Fig. 2), we pre-

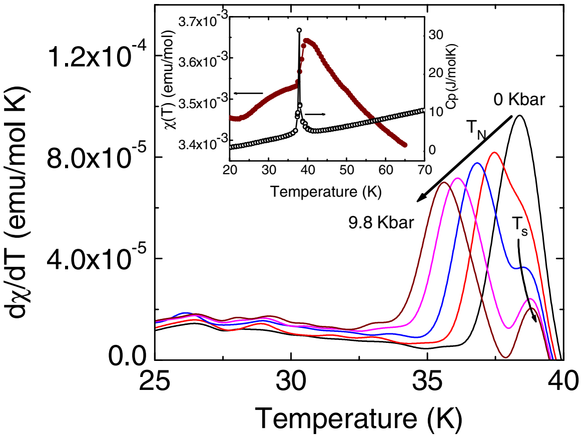

FIG. 5 (color online). Pressure dependence of $\chi(T)$ for Zn[V$_2$]O$_4$. We present the derivative of $\chi(T)$ as the two-peak structure is clearer than in the direct representation. Inset: ambient pressure $\chi(T)$ curve for Zn[V$_2$]O$_4$ measured at $H = 1$ T (left axis) and specific heat (right axis). The drop at ~38 K marks $T_S = T_{OO}$ (see text).

dict a QPT at 7 GPa. Our *ab initio* calculations predict an overlap of the valence and conduction bands, and hence metallic conductivity at ~6.5 GPa for Mg[V$_2$]O$_4$, given no change in the symmetry occurs. Experiments at higher pressure would presumably reach Phase III in a single valence system with direct metal-metal bonding.

In summary, we have determined the pressure dependence of $T_N$ for several $A^{2+}$[V$_2$]O$_4$ spinels to show that as the V-V separation is reduced, there is a breakdown of the localized-electron model [Eq. (1)] for the 3$d$ electrons. The breakdown is first marked by a pressure dependence of the Hubbard $U$ in Mn[V$_2$]O$_4$ and then by long-range ordering of V-V pairs in Zn[V$_2$]O$_4$ and Mg[V$_2$]O$_4$. The simple structure of these materials makes them perfect systems to follow the suppression of the magnetic moment when the itinerant-electron limit is approached. Moreover, if the gap closing predicted by our *ab initio* calculations is confirmed, high pressure studies would allow one to study the strong correlations that develop in the Fermi liquid close to the QPT, in the same system.

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