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Superconductivity, Magnetism and Metal-Insulator Transitions in Some Ternary and Pseudoternary 3d-, 4d- and 5d-Metal Oxides

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Abstract. Electron correlation effects have been found to be particularly important in metallic LiV_2O_4 and possibly $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ ($x > 0.7$), but not in metallic $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ ($x < 0.7$), and they cause the compounds Sr_2IrO_4 and ZnV_2O_4 to be (Mott-Hubbard) insulators. The LiV_2O_4 spinel compound is especially interesting, because the V ions exhibit rather clear local moment ($S = 1/2$) behavior even though the compound is a metal.

1. Introduction

Prior to 1986 when the high superconducting transition temperature (T_c) in layered cuprates with the K_2NiF_4 structure was discovered by Bednorz and Müller [1], the number of distinct superconducting oxide compounds was very small compared to the $\sim 10^3$ superconducting intermetallic compounds and elements. With the exception of the compounds TiO ($T_c < 2.3$ K) and NbO ($T_c < 1.4$ K), all of the superconducting oxides were ternary or higher-component phases grouped in five general classes in which three or more distinct crystallographic sites were occupied: the tungsten bronzes A_xWO_3 ($T_c < 7$ K for $\text{Rb}_{0.1}\text{WO}_3$), the perovskites $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($T_c < 13$ K [2]) and doped SrTiO_3 ($T_c < 1$ K), the clathrate compounds $(\text{Ag}_7\text{O}_8)_x$ ($T_c < 1.5$ K), where X is a monovalent anion, and the cubic spinel compound LiTi_2O_4 ($T_c < 13.7$ K) [3]. Various studies indicated that LiTi_2O_4 is a conventional BCS d-band superconductor [3-5]. The reason that there were so few oxide superconductors is that most oxides are not metallic at low temperatures, a property which up to now is a prerequisite for superconductivity to occur. The 3d-cations in insulating 3d-metal oxides tend to carry local magnetic moments and to order antiferromagnetically. Further, superconductivity was generally found to be absent in compounds containing a crystallographically ordered array of local moments on

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the same sublattice of the structure on which superconductivity resides, irrespective of whether long-range magnetic ordering occurred. The conventional wisdom also held that in seeking new high- T_c (defined at that time as $T_c \geq 20$ K) superconductors, one should try to maximize the density of states at the Fermi energy $D(E_F)$, thereby enhancing the electron-phonon interaction responsible for (conventional) superconductivity. This in turn mandated incorporating transition metals in the compounds and ruled out the perovskite and related structures (such as the newer high- T_c layered cuprates!) because oxygen ions lie directly between nearest neighbor metal ions; hence, if such a material were to be metallic, the electronic bands at the Fermi energy would presumably have to be formed from an intimate mixture of the metal and the oxygen p orbitals, resulting in low $D(E_F)$ and T_c . Indeed, doped SrTiO_3 with the perovskite structure has a maximum T_c of < 1 K [6]. Also, as one attempts to increase the $D(E_F)$ and thereby the electron-phonon interaction, lattice instabilities ultimately set in which limit the attainable electron-phonon interaction and T_c . The relatively high T_c of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($T_c < 13$ K [2]) was anomalous within this phenomenological framework.

In view of the above background, the discovery of superconductivity at ~ 35 K in the layered perovskite-like cuprates by Bednorz and Müller and the subsequent increase in T_c in similar materials by others to the present maximum of ~ 164 K [7] is remarkable. With the advent of these cuprate superconductors, many of the above ideas had to be radically revised. The structures of all the presently known high T_c cuprates contain CuO_2 planes as in the prototypical K_2NiF_4 -type "parent" compound La_2CuO_4 [8]. Features of these compounds of central interest to this paper are that the parent (undoped) insulating member of each system contains Cu^{+2} (d^9) cations with spin $S = 1/2$ which order antiferromagnetically at $T_N \lesssim 550$ K, where strong dynamic short-range antiferromagnetic (AF) order occurs above T_N , and that short-range AF correlations survive in the CuO_2 planes of the doped metallic superconducting compositions [9,10]. It is widely believed that the superconductivity occurs in the CuO_2 layers and therefore develops in the presence of, and is perhaps due to, the short-range AF order of the Cu spins; this is a radical departure from the systematics of superconductivity in conventional superconductors. We have carried out a variety of measurements on other 3d-, 4d- and 5d-transition metal oxides to search for similarities and differences with the properties of the cuprates, in the hope of both elucidating aspects of the properties of the cuprates crucial to their magnetic character and high T_c 's and of finding new high T_c superconductors. In the cases of vanadium oxides, we were interested in $\text{V}^{+4}/\text{V}^{+3}$ (d^1/d^2) systems because they correspond to the electron analogue of the formally $\text{Cu}^{+2}/\text{Cu}^{+3}$ (d^9/d^8) layered cuprates containing 1 or 2 holes in the Cu d-shell. In the following, we give some background and outline our work on some of these systems.

2. Metallic LiV_2O_4

Apart from LiTi_2O_4 , the only other transition metal spinel compound which remains metallic to low temperatures is LiV_2O_4 , as shown from resistivity measurements on single crystals [11]. The formal oxidation state of both the Ti and V cations is +3.5. Since the cations in each compound are crystallographically ordered and equivalent, one cannot assign +3 or +4 oxidation states to particular Ti or V cations, and the non-integral oxidation states demand that the compounds must be metallic, as observed. In the case of the Ti spinel, one formally has $d^{0.5}$ Ti ions. This $1/2$ electron per Ti atom must be itinerant (metallic) in an ionic picture, which has been verified by band structure calculations [5]. For the V spinel, one formally has $d^{1.5}$ V ions. Part of these 1.5 d-electrons/V ion must contribute to the metallic conductivity. In contrast to the temperature (T) independent Pauli paramagnetism

shown by LiTi_2O_4 [3], LiV_2O_4 exhibits a Curie-Weiss magnetic susceptibility $\chi(T) = C/(T - \theta)$, with Curie constant $C \approx 0.47 \text{ cm}^3 \text{ K/mole V}$ and Weiss temperature $\theta = -30$ to -60 K [12], and does not become superconducting above 1.5 K [3]. The Curie constant is expressed as $C = N_A \mu_{\text{eff}}^2 / 3k_B$, where N_A is Avogadro's number, μ_{eff} is the effective moment of a V ion and k_B is Boltzmann's constant. The above C yields $\mu_{\text{eff}} = 1.94 \mu_B/\text{V ion}$, somewhat greater than the value $\mu_{\text{eff}} = g\mu_B[S(S+1)]^{1/2} = 1.73 \mu_B/\text{V ion}$ expected for a spin $S = 1/2$ ion with gyromagnetic factor $g = 2$. Thus, the 1.5 d-electrons per vanadium atom apparently partition into ≈ 0.5 metallic and ≈ 1.0 localized d-electrons. The Curie-Weiss susceptibility and the negative sign of θ correspond to antiferromagnetic interactions between the local vanadium magnetic moments. Remarkably, the 1.5 d electrons originating from the same t_{2g} crystal field levels of the V atom are responsible for both the metallic character and the local moment magnetic behavior.

In contrast to LiV_2O_4 , the spinel compound ZnV_2O_4 , containing V in the d^2 configuration, is a semiconductor with activation energy $\approx 0.20 \text{ eV}$ [13] due to strong electron correlation effects. The ZnV_2O_4 spinel shows antiferromagnetic ordering at $T_N \approx 45 \text{ K}$ with an ordered (staggered) moment at 4.2 K of $\langle \mu \rangle = (0.8 \pm 0.3) \mu_B/\text{V ion}$ [14]. A similar value was obtained for the spinel MgV_2O_4 $[(1.1 \pm 0.1) \mu_B/\text{V ion}]$ [14]. Since the V ions presumably have spin $S = 1$, one would expect $\langle \mu \rangle \approx gS\mu_B \approx 2 \mu_B/\text{V ion}$ for $g \approx 2$; the reason for the discrepancies between the experimental values and the latter estimated value is not clear.

We have carried out $\chi(T)$ and ^7Li nuclear magnetic resonance (NMR) measurements on LiV_2O_4 to further characterize its magnetic properties [15]. The sample was prepared using solid state reaction [3,4]. The lattice parameter was found to be $8.235 \text{ \AA}$, in agreement with previous reports [13]. The $\chi(T)$ measurements were carried out with a commercial SQUID magnetometer. The ^7Li NMR measurements were performed with a coherent pulse Fourier Transform spectrometer at variable frequency (applied magnetic field $H = 10 - 82 \text{ kG}$) from 4.2 to 300 K .

As shown in Fig. 1, the molar susceptibility $\chi_M(T)$ was found to follow a Curie-Weiss law from 10 K to 300 K , with Curie constant $C = 0.535 \text{ cm}^3 \text{ K/mole V}$, corresponding to $\mu_{\text{eff}} = 2.06 \mu_B/\text{V atom}$, and Weiss temperature $\theta = -35.4 \text{ K}$, comparable to previous results [12].

The ^7Li NMR linewidth is found to be field-dependent, indicating that the broadening is inhomogeneous, arising from a distribution of local fields due to the presence of localized moments at the V site. Both the linewidth, $\Delta\nu$, and the line shift, K , are temperature dependent and are related to χ_M as shown in Figs. 2(a-d). From theory, one expects

$$\Delta\nu = 2(M_2^{\text{dip}})^{1/2} = 2[M_2^{\text{dip}} + (A_{\text{hf}} \chi_M \gamma_n H)^2]^{1/2}, \quad (1)$$

where M_2^{dip} is the Van Vleck nuclear dipolar second moment, A_{hf} is the nuclear-electron dipolar hyperfine interaction and $\gamma_n = 2\pi(1655 \text{ Hz/Gauss})$ is the gyromagnetic ratio of the ^7Li nucleus. The theoretical estimated value of M_2^{dip} is $8.4 \times 10^6 \text{ Hz}^2$, which compares very well with the value $5.5 \times 10^6 \text{ Hz}^2$ obtained from a linear fit to the data in Fig. 2(b). Theoretically, $A_{\text{hf}} = \sum_j (1 - 3\cos^2\theta_{ij})/r_{ij}^3$, where the sum runs over all V_j local moments around a given Li nucleus i . The sum calculated over 32 unit cells yields $A_{\text{hf}} = 0.174/\text{\AA}^3 = 0.104 \text{ mole/cm}^3$, which is in reasonable agreement with the experimental value $A_{\text{hf}} = 0.043 \text{ mole/cm}^3$ obtained from the linear fit to the data in Fig. 2(b).

The line shift K of the ^7Li NMR line varies linearly with χ_M as shown in Fig. 2(d). For a paramagnetic shift due to local moments, one has

$$K = K_0 + \bar{A}_{hf} \chi_M \quad (2)$$

where K_0 is the Knight shift originating from the conduction electrons and $\bar{A}_{hf}$ is the hyperfine interaction between ^7Li nuclei and V paramagnetic ions. From a linear fit to the data in Fig. 2(d), one obtains $K_0 = 0.001\%$ and $\bar{A}_{hf} = 0.144$ mole/cm³. The value for K_0 is very small, which is quite reasonable for ^7Li in view of the very small contact hyperfine interaction (K_0 of ^7Li in Li metal is only 0.026%). Averaged over the powder distribution, $\bar{A}_{hf}$ should be zero for paramagnetic ions with isotropic g factor. The value of $\bar{A}_{hf}$ could be explained either as a dipolar interaction with local magnetic moments having an anisotropic g factor or with a small transferred hyperfine interaction between V d-orbitals and Li nuclei.

The T dependence of the nuclear spin-lattice relaxation rate T_1^{-1} for ^7Li in LiV_2O_4 , shown in Fig. 2(e), indicates that the relaxation is dominated by the interaction with local paramagnetic moments. The contribution from the conduction electrons, estimated using the K_0 value above, is given by the Korringa relation $(T_1 T)^{-1} = S^{-1} K_0^2 = 5 \times 10^{-5} \text{ sec}^{-1} \text{ K}^{-1}$ and is thus entirely negligible compared with the data in Fig. 2(e). For ^7Li , the constant $S = (\gamma_e/\gamma_n)^2 h / (8\pi^2 k_B) = 1.8 \times 10^{-6} \text{ sec}^{-1} \text{ K}^{-1}$, where γ_e is the electronic gyromagnetic ratio and h is Planck's constant. The contribution to T_1^{-1} due to paramagnetic ions is $(T_1 T)^{-1} = \gamma_n^2 \bar{A}_{hf}^2 k_B \sum_q \text{Im} \chi^+(q, \omega_L) / \omega_L$, where q is the wavevector and $\omega_L = 2\pi\gamma_n H$ is the Larmor angular frequency. In the limit of high T where correlations among paramagnetic ions are negligible, this reduces to

$$\frac{1}{T_1 T} = \frac{\gamma_n^2 \bar{A}_{hf}^2 N_A k_B \chi_M}{\omega_e} \quad (3)$$

where the exchange frequency ω_e is given by $\omega_e^2 = (8\pi^2/3) J^2 z S(S+1)/h^2$ and z is the number of nearest neighbor V ions to a V ion. The AF V-V exchange interaction constant is $J = 3k_B \theta / [2zS(S+1)] = -11.6 \text{ K}$, using $z = 6$, $S = 1/2$ and Weiss temperature $\theta = -35 \text{ K}$ from above, yielding $\omega_e = 5 \times 10^{12} \text{ rad/sec}$. Inserting this ω_e and the above $\bar{A}_{hf}$ into Eq. (3) yields $(T_1 T)^{-1} = 35 \chi_M (\text{sec}^{-1} \text{ K}^{-1})$. As shown in Fig. 2(f), this prediction, represented by the dashed line, gives good agreement with the data in the limit of high T where one expects weak correlation among the localized V moments. The much stronger relaxation observed in Figs. 2(e,f) at low T must arise from AF fluctuations at a wavevector $q = q_{AF}$ not included in Eq. (3) which involves only the $q = 0$ uniform susceptibility, χ_M , and is thus only correct as long as all q -components of the susceptibility are equal to the $q = 0$ uniform one. It should be noted that a critical behavior $(T_1 T)^{-1} \propto (T - T_N)^{-n}$ expected for a divergent staggered susceptibility does not fit the experimental data in Fig. 2(e) for any reasonable choice of parameters. On the other hand a good fit to the data in Fig. 2(f) is obtained with an empirical quadratic dependence: $(T_1 T)^{-1} = 6600 \chi_M^2 (\text{sec}^{-1} \text{ K}^{-1})$, as shown by the solid curve in the figure. The implications of this behavior, which is not borne out in any theory of critical slowing down of spin fluctuations, are not understood.

We have thus established that the V ions in metallic LiV_2O_4 do indeed carry a local magnetic moment and that these moments are *antiferromagnetically* coupled. These moments evidently have spin $S = 1/2$. Electron correlations are manifested not only in the existence of the local V moments but also in the occurrence of AF spin fluctuations which strongly affect the Li nuclei spin-lattice relaxation rate below $\sim 150 \text{ K}$. On the other hand, the effective moment/V ion from the $\chi(T)$ measurements is about 15% larger than that expected for $g = 2$ and $S = 1/2$. This implies that the V spins have a *ferromagnetic* coupling to the conduction electron

spins which would increase the g value of the V ions beyond $g = 2$. Further experiments are necessary to clarify this issue.

Our results are consistent with those of ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopy measurements on LiV_2O_4 which indicated that $D(E_F)$ is much lower than predicted from band structure calculations (for LiTi_2O_4) [16]. This observation is indicative of electron correlation effects and the failure of the (weakly correlated electron) band picture. The authors analyzed their data in terms of a localized picture in which the V ion fluctuates between the d^1 and d^2 configurations on a time scale longer than that of photoemission ($\sim 10^{-15}$ sec). From analysis of their data, the authors obtained a value for the intra-atomic Coulomb energy $U \sim 2$ eV, which is on the same order as that previously estimated for VO_2 and V_2O_3 . The authors suggested that the long-range Coulomb interaction could also be important to the suppression of $D(E_F)$.

3. The Metal-Insulator Transition in $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$

The $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ ($0 \leq x \leq 1$) system, with the three-dimensional perovskite structure or a distorted variant thereof, was first investigated more than 30 years ago [14] and is currently still of interest because of its striking similarities to the cuprate high T_c superconductors. The end-member SrVO_3 is a metallic Pauli paramagnet [17,18] whereas the other one, LaVO_3 , is an antiferromagnetic insulator with $T_N \approx 140$ K [19]. A composition-induced metal-to-insulator (M-I) transition occurs with increasing x at $x \approx 0.8$ [20]. These features are similar to those of the cuprates noted in Section 1. For example, in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system [9], the $x = 0$ member is an AF insulator with $T_N = 325$ K. The system becomes metallic and superconducting for $0.1 \leq x \leq 0.25$. Upon increasing x further, the system is not superconducting and behaves more like a normal d-band metal. Thus the change in composition from La_2CuO_4 to the heavily Sr-doped non-superconducting metallic phase apparently spans the theoretically difficult region from the limit of strong correlation (i.e., local moments) to the limit corresponding to conventional band theory. We carried out combined crystallographic, $\chi(T)$ and ^{51}V NMR measurements on the $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ ($0.1 \leq x \leq 1$) system, to clarify the importance of electron correlations in the metallic phase and to the M-I transition [21]. A complete solid solution was found to form between $x = 0$ and 1, in agreement with [22]. Also in agreement with previous work [20], our resistivity versus temperature measurements indicated the M-I transition to occur at $x \approx 0.8$.

The T-dependent molar susceptibility $\chi_M(T)$ of $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ is plotted for different compositions x in Fig. 3(a). The onset of long-range AF order is evident for $x = 0.9$ and 1.0 via kinks in the data at $T_N \approx 105$ K and 140 K, respectively. From this figure, $\chi_M(T)$ is seen to be nearly independent of T , even for the AF compositions $x > 0.8$ for $T > T_N$, except for a small low-T Curie-like upturn presumably due to paramagnetic impurities. The susceptibility at 300 K corrected for the Curie term, $\chi_M^{\text{corr}}(300 \text{ K})$, is plotted versus x in Fig. 3(b). A smooth variation in $\chi_M^{\text{corr}}(300 \text{ K})$ with x is seen across the whole composition range, with no obvious discontinuity near $x = 0.8$ at which the M-I transition occurs, akin to the behavior seen across the M-I transition in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system [9].

From the ^{51}V NMR measurements, the Knight shift K_0 was found to be independent of both temperature and composition in the metallic phase with $x \leq 0.7$. The former result is expected for a metal, but the latter is anomalous. For typical metals, one expects K_0 to scale with χ_M in Fig. 3(b), which clearly does not occur. The variation of the ^{51}V spin-lattice relaxation rate T_1^{-1} with T in the metallic phase is shown in Fig. 4, where the Korringa relation $T_1 T = \text{constant}$, independent of x , is found to hold within the error limits. Thus the Knight shift and spin-lattice

relaxation rate measurements are consistent with each other according to the Korringa relation, and show no evidence of spin correlations in the metallic phase such as observed above for LiV_2O_4 and cited above for the metallic side of the M-I transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

To understand why $K_0(x)$ and $(T_1T)^{-1}(x)$ are independent of x in the metallic phase of $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ in contrast to the strong composition dependence of $\chi_M(x)$, detailed combined analysis of these three measurements were carried out which reconciled these results [21]. With increasing x , the d-band band structure density of states was found to be nearly independent of x , whereas the ferromagnetic Stoner exchange enhancement factor increases strongly with x , resulting in the observed composition dependence of χ and composition independence of K_0 and $(T_1T)^{-1}$.

4. 4d- and 5d-Transition Metal Oxides with the K_2NiF_4 Structure

As noted in Section 1, the parent compounds of the high T_c cuprate superconductors are two-dimensional spin 1/2 Heisenberg antiferromagnets on a square lattice, and short-range AF order persists in the superconducting compositions. In order to deepen our understanding of the magnetic properties of these cuprates, and to expand the range of materials which might exhibit high T_c superconductivity, we are investigating the structural and magnetic properties of transition metal oxides which would be expected to have similar magnetic properties. Here we discuss our work on the 5d oxide Sr_2IrO_4 [23,24] and the 4d oxide Sr_2RhO_4 [24] which crystallize in the K_2NiF_4 structure [25,26].

The electronic configurations of the Ir^{+4} and Rh^{+4} ions are $[\text{Xe}]4f^{14}5d^5$ and $[\text{Kr}]4d^5$, respectively. From the large crystalline electric fields at the d-ion site and the large spin-orbit couplings, we expect the Ir and Rh ions in Sr_2IrO_4 and Sr_2RhO_4 to be in the low-spin configuration t_{2g}^5 , with the ground state being 2T_2 . This state is split by spin-orbit coupling and the tetragonal crystal field into three Kramers doublets. Thus, the ground states of Sr_2IrO_4 and Sr_2RhO_4 are expected to be spin 1/2 Kramers doublets, where the unpaired spin occupies a half-filled d_{xy} orbital, similar to La_2CuO_4 where the Cu^{+2} hole spin resides in a half-filled e_g ($d_{x^2-y^2}$) orbital.

Samples of Sr_2IrO_4 and Sr_2RhO_4 were prepared using standard solid state synthesis techniques. Neutron and high-resolution synchrotron x-ray powder diffraction data were obtained at Oak Ridge National Laboratory and Brookhaven National Laboratory, respectively. Magnetization measurements were made with a Quantum Design SQUID magnetometer and an Oxford Instruments Faraday magnetometer. Electrical resistivity measurements indicate that Sr_2IrO_4 is an insulator [23], while Sr_2RhO_4 showed metallic behavior below 150 K [26].

The diffraction data for Sr_2IrO_4 and Sr_2RhO_4 showed the presence of superstructure reflections which could be indexed on a unit cell of dimensions $2^{1/2}a \times 2c$, where a and c are the tetragonal lattice parameters for the K_2NiF_4 -type $I4/mmm$ cell [23,24]. A structure was proposed [23,24], shown in Fig. 5, in which the IrO_6 and RhO_6 octahedra are rotated about the crystallographic c axis by about 11° and 9.7° , respectively, thereby reducing the space group symmetry from $I4/mmm$ to $I4_1/acd$, similar to the structural distortion observed in K_2NiF_4 -type Ca_2MnO_4 [27]. This distortion contrasts with that found below 530 K in La_2CuO_4 , in which the CuO_6 octahedra are rotated in a staggered fashion about the (110) tetragonal axis in the a - b plane.

The $\chi(T)$ for Sr_2IrO_4 is shown in Fig. 6(a) [23]. Below $T_N \approx 250$ K, the susceptibility increases dramatically. Measurements of magnetization vs. field isotherms revealed that a small ferromagnetic (FM) magnetization developed below T_N as shown in Fig. 6(b) for data taken at 5 K. The magnitude of the remanent

saturation magnetization in Fig. 6(b) is $M_s \approx 0.30 \text{ G cm}^3/\text{g} = 0.023 \mu_B/\text{Ir atom}$. This M_s is much smaller than the ordered moment $\langle \mu \rangle = gS\mu_B \approx 1 \mu_B$ expected for FM alignment of an atom with spin $1/2$ and $g \approx 2$. Furthermore, by analogy to the layered cuprate parent compounds with similar structures, one expects AF rather than FM order. Single crystal magnetization measurements indicate that the FM moment is aligned in the c -direction [24]. We conclude that the magnetic ordering below T_N in Sr_2IrO_4 is most likely weak ferromagnetism in which the basic AF magnetic structure is slightly canted parallel to the c -axis. This canting presumably arises from the Dzyaloshinsky-Moriya exchange interaction between the Ir ions which is allowed in the distorted structure.

In contrast, weak ferromagnetism is not seen in Sr_2RhO_4 , despite the fact that the structures are similar. However, $\chi(T)$ data do show a broad peak at $\approx 200 \text{ K}$, possibly indicating the presence of 2D short range AF order [26]. Fluorine substituted phases of the type $\text{Sr}_2\text{RhO}_{4-x}\text{F}_x$ were also synthesized for $0 \leq x \leq 0.15$ [24]. These compounds showed metallic behavior and weak ferromagnetism at low T .

Unlike Sr_2IrO_4 , the K_2NiF_4 -type compound Sr_2RuO_4 is a good metal (at least parallel to the a - b plane) [28] showing (nearly) temperature independent Pauli paramagnetism [29, 30]. The electronic configuration of Ru^{+4} is $[\text{Kr}]4d^4$. A crystallographic, resistivity and magnetic susceptibility study was recently reported for the solid solution $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ which was found to show an insulator-to-metal transition with increasing x at $x \approx 0.7$ [30]. The lattice parameters versus composition show distinct changes in slope upon traversing the insulator-to-metal transition. In the insulating compositions, the Ru ion was found to have spin $S = 1$ (assuming $g \approx 2$), but the Ru local moment is apparently progressively destroyed in the metallic phase as x increases above $x \approx 0.7$.

5. Concluding Remarks

Among the compounds discussed here, electron correlation effects have been found to be particularly important in the metallic compounds LiV_2O_4 and possibly $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ ($x > 0.7$), but not in metallic $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ ($x < 0.7$), and they cause the compounds Sr_2IrO_4 and ZnV_2O_4 to be (Mott-Hubbard) insulators. The LiV_2O_4 spinel compound is especially interesting, because the V ions exhibit rather clear local moment ($S = 1/2$) behavior even though the compound is a metal. Our ^7Li NMR experiments indicate that antiferromagnetic spin correlations occur between the V ions, consistent with the negative sign of the Weiss temperature from magnetic susceptibility measurements.

The local moment behavior of the V ions and the AF correlations between them are qualitatively the same in LiV_2O_4 as those of the Cu^{+2} ions ($S = 1/2$) in the cuprate high temperature superconductors, yet LiV_2O_4 is not superconducting above 1.5 K . However, at least three characteristics of the cuprates are lacking. First, the V ions have a three-dimensional structure in contrast to the square lattice layered structure of the Cu ions. Second, the exchange coupling between the V ions ($|J| \approx 12 \text{ K}$) is more than 100 times weaker than between the Cu ions (1500 K). Third, the oxygen $2p$ orbitals are $\approx 2 \text{ eV}$ below the Fermi energy E_F in LiV_2O_4 [5], whereas they overlap E_F in the cuprates; i.e., electronic conduction occurs at least in large measure on the oxygen sublattice of the cuprates. Future work will hopefully determine whether one or more of these features are crucial to high temperature superconductivity.

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Figure Captions

Fig. 1. Inverse molar magnetic susceptibility χ_M^{-1} versus temperature T for LiV_2O_4 . The solid line is a linear least square fit to the data (Curie-Weiss law) [15].

Fig. 2. ^7Li NMR line width at half maximum measured at 17 MHz ($\Delta\nu$), paramagnetic line shift measured at 17 MHz and 135 MHz, and nuclear spin-lattice relaxation rate T_1^{-1} divided by T , $(T_1T)^{-1}$, versus temperature T [(a), (c), (e)] and versus molar susceptibility χ_M [(b), (d), (f)], respectively, for LiV_2O_4 . In (b), the solid curve is a fit of Eq. (1) to the data. In (d), the solid line is a fit of Eq. (2) to the data. In (f), the dashed line is the calculated dependence at high T in Eq. (3), and the solid curve is an empirical fit $(T_1T)^{-1} = 6600\chi_M^2 (\text{sec}^{-1} \text{K}^{-1})$ [15].

Fig. 3. (a) Molar magnetic susceptibility χ_M for $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ versus temperature T for different La contents x ; (b) Molar magnetic susceptibility corrected for small Curie-Weiss impurity terms, χ_M^{corr} , versus La content x at 300 K [21].

Fig. 4. ^{51}V nuclear spin-lattice relaxation rate $1/T_1$ versus temperature T for metallic samples of $\text{Sr}_{1-x}\text{La}_x\text{VO}_3$ with $x \leq 0.6$ [21].

Fig. 5. Structure of Sr_2IrO_4 ($I4_1/acd$) showing the IrO_6 octahedra rotation pattern in each layer of height z along the c -axis of the unit cell. The square superimposed on each figure is the unit cell in the a - b plane. The c axis is perpendicular to the page [23].

Fig. 6. (a) Molar magnetic susceptibility versus temperature T and (b) magnetization versus applied magnetic field hysteresis loop at 5 K, for Sr_2IrO_4 [23].

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Figure 1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Figure 2(a)

Figure 2(b)

Figure 2(c)

Figure 2(d)

Figure 2(e)

Figure 2(f)

Figure 3(a)

Figure 3(b)

Figure 4

$$z = 7/8$$

$$z = 5/8$$

$$z = 3/8$$

$$z = 1/8$$

Figure 5

Figure 6

Oak Ridge – Knoxville Route Map

OAK RIDGE -- ORNL MAP ON REVERSE SIDE

ATHENS, GA

CHATTANOOGA