

These considerations lead to the following predictions for perovskites containing B cations having two localized outer electrons: At high temperatures the magnetic susceptibility is temperature-dependent; antiferromagnetic order sets in below a T_N that increases sharply with the covalency parameter λ_π ; cubic crystals ($\tilde{D}_{ij} = 0$) have collinear spins and should exhibit a tetragonal ($c/a < 1$) \rightleftharpoons cubic transition at T_N whereas orthorhombic crystals having space group Pbnm ($\tilde{D}_{ij} \neq 0$) may exhibit a parasitic ferromagnetism in the interval $T_t < T < T_N$, where $T_t \leq T_N$ marks an O' -orthorhombic ($c/\sqrt{2} < a \leq b$) \rightleftharpoons O-orthorhombic ($a < c/\sqrt{2} < b$) transition as a result of a cooperative spin-orbit-coupling distortion below T_t that orders the principal spin component along the c-axis, making $\tilde{D}_{ij} = 0$. Electrical conductivity has a semiconducting temperature dependence with an activation energy

$$\epsilon_t = \frac{1}{2}U + \epsilon_a \quad (13)$$

for intrinsic material. Here ϵ_a comes from an activated mobility for localized charge carriers.

As λ_π increases, the interactions become stronger; and for large λ_π the transfer energies of Equation (7) become so large that the assumption of localized electrons breaks down. For large enough λ_π , screening effects make $U \approx 0$ and, in the tight-binding approximation, the width of the allowed energy band is

$$w_b \sim b_{ij} \sim \lambda_\pi^2 \quad (14)$$

In this limit there is no spontaneous magnetism of the two outer d electrons per B cation, only a temperature-independent Pauli paramagnetism due to a half-filled $J = 3/2$ band. Given a $U = 0$, superconducting diamagnetism should appear below a transition temperature T_{cs} . However, as λ_π decreases, a $U \neq 0$ begins to appear, first quenching T_{cs} [9] and then introducing a temperature-dependent susceptibility χ_m and a splitting in two of the $J = 3/2$ band [10]. The energy gap between the two half-bands is roughly

$$E_g \approx \left(U^2 + \frac{1}{4} w_b^2 \right)^{1/2} - \frac{1}{2} w_b \quad (15)$$

and charge-carrier mobilities are not activated ($\epsilon_a = 0$). Where $E_g \neq 0$, further stabilization can be achieved at low temperatures by a spontaneous antiferromagnetic ordering, since this would increase the energy discontinuity about the Fermi energy [11]. Thermal excitation across the gap decreases the stabilization energy due to magnetic

order, and the ordering temperature T_N should decrease with E_g and hence with increasing λ_π .

Figure 2 shows a schematic b_{ij} - T phase diagram, where the electrons are localized for $b_{ij} < b_c$ and spontaneous antiferromagnetism occurs for $b_{ij} < b_m$. Since both b_c and b_m are determined by a critical value of the ratio b_{ij}/U , where U is anticipated from Equation (8) to decrease rapidly with increasing b_{ij} , the critical parameters b_c and b_m should be sharply defined. Finally note that in the collective-electron domain $b > b_c$, any spontaneous crystallographic distortions would be due to our ordering among collective electrons that either increased or introduced an energy discontinuity at the Fermi surface [12]. With an anion intermediary, spontaneous antiferromagnetic order is energetically more favorable than cationic clustering, and no spontaneous crystallographic distortion is anticipated below T_N .

The interval $b_c < b < b_m$ is clearly transitional between the conditions for localized electrons, where crystal-field theory is applicable, and the conditions for $U \approx 0$, where conventional band theory is applicable. It is only in this interval that the difficult problem of correlations among collective electrons must be introduced. It is therefore of great interest to know how extensive this transitional region is, or whether there is a first-order phase change from $b < b_c$ to $b > b_m$, as first suggested by Mott [13] for the case of interactions between impurity centers in doped semiconductors.

Application of the Electronic Phase Diagram

The compounds of Table 2 are listed in the order of decreasing $b_{ij} \sim \lambda_\pi^2$. The argument for this ordering goes as follows: There should be greater λ_π for B cations of larger formal charge (4+ vs 3+) and for 4d orbitals vs 3d orbitals given the same formal charge. Thus λ_π is greater for Mo^{4+} ions than for Cr^{4+} ions, and for Cr^{4+} ions than for V^{3+} ions. Further, the anionic p_π orbitals not only π -bond with the B cations, but also σ -bond with the A cations. This produces a competition for covalent mixing with the anionic p_π orbitals, a competition between the B-cation orbitals of t_{2g} symmetry and the A-cation sp^3 orbitals. The more basic (more ionic) the A cation, the less it competes with the B-cation covalency and hence the larger λ_π . Therefore λ_π increases in the series $A = \text{Pb}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}$ and in the series $A = \text{Y}^{3+}, \text{La}^{3+}$. The most subtle changes in λ_π should occur within the series $A^{2+}\text{MoO}_3, A^{2+}\text{CrO}_3$, or $A^{3+}\text{VO}_3$. The decrease in λ_π on going from PbCrO_3 to LaVO_3 is primarily due to a reduced B-cationic charge. The larger formal charge on La^{3+} vs Pb^{2+} , which