TABLE 2

Physical Properties of Perovskites with d^2 Configuration at the B Cations

Compound	$T_N(^oK)$	$d\rho/dT$[b]	Symm. 300°K	Remarks	Refs.
$BaMoO_3$	Pauli[a]	> 0	Cubic		15
$SrMoO_3$	Pauli[a]	> 0	Cubic		15
$CaMoO_3$	Pauli[a]	> 0	Ortho.		
$SrCrO_3$	Pauli[a]	> 0	Cubic		3
$CaCrO_3$	90	< 0	Ortho.	$dT_N/dP = -0.23^oK/kbar$	
$PbCrO_3$	240	< 0	Cubic	Collinear Type-G order $T < T_N$	2
$LaVO_3$	137	< 0	(Cubic)	Tet. $(c/a < 1) \rightleftharpoons$ Cubic at T_N	14
YVO_3	110	< 0	Ortho.	DTA anomaly at $T_t = 73^oK$	14

a. Pauli = temperature-independent χ_m and no spontaneous magnetic order.

b. ρ = electrical resistivity: Metallic ($d\rho/dT > 0$) vs semiconducting ($d\rho/dT < 0$).

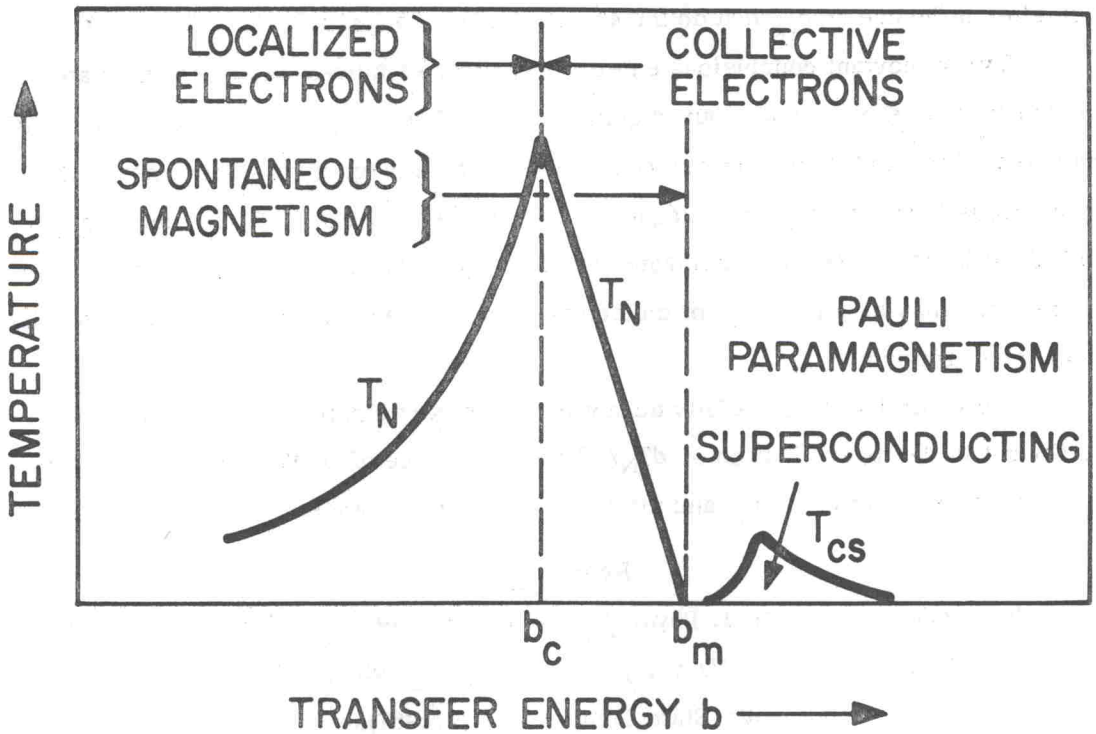

FIG. 2

Electronic phase diagram for one electron per interacting orbital. Semiconducting for $b_{ij} < b_m$, metallic for $b_{ij} > b_m$.

introduces more covalency in the A-O bond, is largely compensated by the fact that lanthanum is far to the left of lead in the periodic table.

Comparison of Table 2 with the phase diagram of Fig. 2 places $SrCrO_3$ and $AMoO_3$ (A = Ca, Sr, Ba) in the domain $b_{ij} > b_m$, $PbCrO_3$ and $CaCrO_3$ in the transitional domain $b_c < b_{ij} < b_m$, and the two vanadates $LaVO_3$, YVO_3 in the localized-electron domain $b_{ij} < b_c$. The fact that $PbCrO_3$ remains cubic to lowest temperatures, even though it has a collinear type-G antiferromagnetic order [2], is consistent with collective d electrons. By contrast, $LaVO_3$ exhibits a tetragonal ($c/a < 1$) to cubic (or O′-orthorhombic to O-orthorhombic, where distrotions toward orthorhombic symmetry are very small) transition [14], which is characteristic of spin-orbit coupling and localized d electrons having collinear spins. YVO_3, which does not undergo a crystallographic transition at T_N, exhibits a definite DTA anomaly at $73^oK < T_N$, which suggests the anticipated O′-orthorhombic to O-orthorhombic transition. Finally, a $dT_N/dP < 0$ for $CaCrO_3$ is consistent with Fig. 2 and $b_c < b_{ij} < b_m$, since b_{ij} should increase with a pressure-induced decreasing lattice parameter. (Changes in the lattice parameter by chemical means, as in $CaCrO_3$ vs $SrCrO_3$, have a smaller influence on b_{ij} than do the accompanying changes in A-O covalency.)

Two important conclusions emerge from these studies: (1) An intermediate domain $b_c < b_{ij} < b_m$ exists, but is quite narrow. The compounds $PbCrO_3$ and $CaCrO_3$ may be said to exhibit spontaneous collective-electron magnetism in contrast to the spontaneous localized-electron magnetism of YVO_3 and $LaVO_3$. (2) The fact that $CaCrO_3$ exhibits parasitic ferromagnetism demonstrates that antisymmetric exchange interactions may be a property of collective-electron magnetism as well as of localized-electron magnetism.

We would like to gratefully acknowledge the participation of N. Menyuk and K. Dwight in the determination of dT_N/dP, the assistance of D. Batson and T. Hilton in the preparation of $CaCrO_3$, and the thermogravimetric analysis by C. Anderson.

References

1. J. B. Goodenough, J. Appl. Phys. 37, 1415 (1966); 39, 403 (1968).
2. W. L. Roth and R. C. DeVries, J. Appl. Phys. 38, 951 (1967).
3. B. L. Chamberland, Solid State Comm. 5, 663 (1967).
4. R. C. DeVries and W. L. Roth, J. Am. Ceramic Soc. 51, 72 (1968).
5. S. Geller and E. A. Wood, Acta Cryst. 9, 563 (1956).