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NEW PEROVSKITE CaCrO3

Physica	l Properti	es of Perovs	skites with d ² Configuration at the B Cations	
Compound	т _N (⁰ К)	dp/dT ^b	Symm. 300 ⁰ K Remarks Re:	fs
BaMoO ₃	Pauli ^a	> 0	Cubic 1	5
SrMoO ₃	Pauli ^a	> 0	Cubic 1	5
CaMoO ₃	Pauli ^a	> 0	Ortho.	
SrCrO3	Pauli ^a	> 0	Cubic	3
CaCrO ₃	90	< 0	Ortho. $dT_N/dP = -0.23^{\circ}K/kbar$	
PbCrO ₃	240	< 0	Cubic Collinear Type-G order T < T _N	2
LaV O3	137	< 0	(Cubic) Tet. $(c/a < 1) \neq$ Cubic at T_N 1.	4
YVO3	110	< 0	Ortho. DTA anomaly at $T_t = 73^{\circ}K$ 14	4

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

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



TABLE 2

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 SrCrO₃ and A MoO₃ (A = Ca, Sr, Ba) in the domain $b_{ij} > b_m$, PbCrO₃ and CaCrO₃ in the transitional domain $b_c < b_{ij} < b_m$, and the two vanadates LaVO₃, YVO₃ in the localized-electron domain $b_c < b_c$. The fact that PbCrO₃ remains cubic to lowest temperatures, even though it has a collinear type-G antiferromagnetic order [2], is consistent with collective d electrons. By contrast, LaVO₃ 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. YVO₃, which does not undergo a crystallographic transition at T_N , exhibits a definite DTA anomaly at 73°K < T_N , which suggests the anticipated O'-orthorhombic to O-orthorhombic transition. Finally, a $dT_N/dP < 0$ for CaCrO₃ 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 CaCrO₃ vs SrCrO₃, 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 PbCrO₃ and CaCrO₃ may be said to exhibit spontaneous collective-electron magnetism in contrast to the spontaneous localized-electron magnetism of YVO₃ and LaVO₃. (2) The fact that CaCrO₃ exhibits parasitic ferromagnetism demonstrates that antisymmetric exchange interactions may be a property of collective-electron magnetism as well as of localizedelectron magnetism.

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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).

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- 3. B. L. Chamberland, Solid State Comm. 5, 663 (1967).
- 4. R. C. DeVries and W. L. Roth, J. Am. Ceranic Soc. 51, 72 (1968).
- 5. S. Geller and E. A. Wood, Acta Cryst. 9, 563 (1956).