

The effect of hydrostatic pressure on T_N was obtained from a vibrating-coil magnetometer equipped with a special pressure vessel made of a diamagnetic beryllium-copper alloy and using helium as the pressure-transmitting medium:

$$dT_N/dP = -0.23^\circ\text{K/kbar} \quad \text{up to 6 kbar.} \quad (2)$$

The Néel temperature was assumed to be given by the sharp increase with decreasing temperature in χ_m due to the appearance of parasitic ferromagnetism.

Phenomenological Phase Diagram

Localized d electrons are described by crystal-field theory. For a single electron outside closed-shell cores, the zero-order potential is spherical. This leads to wave functions of the form

$$f_{\ell m} = R_\ell(r) Y_\ell^m(\theta, \phi) \quad (3)$$

where $\ell = 2$ for outer d electrons. The spherical potential is perturbed by the cubic crystalline fields and by covalent mixing. Octahedral-site symmetry splits the atomic orbitals into the twofold-degenerate e_g orbitals directed toward near-neighbor anions and the more stable, threefold-degenerate t_{2g} orbitals directed toward near-neighbor A cations. After covalent mixing with the near-neighbor s and p orbitals, the crystal-field orbitals of e_g and t_{2g} symmetry are

$$\psi_e = N_\sigma(f_e + \lambda_\sigma \phi_\sigma), \quad \psi_t = N_\pi(f_t + \lambda_\pi \phi_\pi + \lambda_A \phi_A) \quad (4)$$

where N_σ, N_π are normalization constants, $\lambda_\sigma, \lambda_\pi, \lambda_A$ are covalent-mixing parameters, and $\phi_\sigma, \phi_\pi, \phi_A$ are the symmetrized anionic sp_σ , anionic p_π^2 and A-cationic sp^3 orbitals. (Covalent mixing with s, p orbitals on next-near-neighbor B cations would add a smaller fourth term to ψ_t .) Although the crystalline fields partially quench the orbital angular momentum, spin-orbit coupling splits the energy E_t of the states of t_{2g} symmetry into a more stable, four-fold degenerate (including spin) level $E_{3/2}$ and a less stable, two-fold degenerate level $E_{1/2}$, where

$$E_{1/2} - E_{3/2} = 2k_c \lambda \quad (5)$$

Here λ is the atomic parameter entering the spin-orbit-coupling energy $\lambda \underline{L} \cdot \underline{S}$, and k_c is a large fraction (~ 0.9) reflecting the increase in $R(r)$ due to covalent mixing.

In the case of two, localized outer d electrons, intra-atomic exchange splits the states of different spin, α and β , and the ground state corresponds to the fivefold degenerate energy E_2 for states with total angular momentum $J = L + S = 2$, where

$$E_1 - E_2 = 3k \frac{\lambda}{c} \quad (6)$$

Interactions between near-neighbor B cations arise via the matrix elements

$$b_{ij} \equiv (\psi_i, h\psi_j) \approx \epsilon(\psi_i, \psi_j) \sim \epsilon N_{\pi}^2 \lambda_{\pi}^2 \quad (7)$$

where h is the change in the localized-electron potential energy of the B cation at \underline{R}_i that is due to the presence of a B cation at \underline{R}_j . These matrix elements represent a gain in energy due to an electron transfer from \underline{R}_i to \underline{R}_j . However, such an electron transfer costs an electrostatic energy

$$U = (e^2/r_{12}) \exp(-\xi r_{12}) \quad (8)$$

where the screening parameter $\xi = \xi(b)$ increases with increasing b_{ij} . Second-order perturbation theory gives the superexchange interaction energy [6, 7]

$$\mathcal{K}_{\text{ex}} = - \sum_{ij} \{ J_{ij} S_i \cdot S_j + D_{ij} S_i \times S_j \} \quad (9)$$

where the dominant contribution to the isotropic exchange parameter is

$$J_{ij} \approx - 2b_{ij}^2 / U \quad (10)$$

The minus sign enters because electron transfer conserves the total angular momentum $\underline{j} = \underline{\ell} + \underline{s}$: With half-filled $J=2$ states, the Pauli exclusion principle excludes electron transfer between states of parallel spin, and antiferromagnetic coupling is stabilized. Further, the antiferromagnetic ordering temperature is

$$T_N \sim J_{ij} \sim \lambda_{\pi}^4 / U \quad (11)$$

where U decreases with increasing λ_{π} . The existence of an anisotropic exchange parameter [7]

$$D_{ij} \approx (\Delta g/g) J_{ij} \quad (12)$$

introduces parasitic ferromagnetism, but does not alter Equation (11). Here Δg is the variation of the spectroscopic splitting factor from $g = 2$. Finally, spin-orbit coupling and collinear spins below T_N order the occupied $J = 2$ orbitals so as to give a cooperative distortion of a cubic crystal to tetragonal ($c/a < 1$) symmetry [8].