

degenerate. However, the energy of the ion will be lowered if the ion displaces itself with respect to the surroundings, thereby creating a noncubic potential such as (24). Such a spontaneous displacement is known as a **Jahn-Teller effect** and is often large and important, particularly with the Mn^{3+} and Cu^{2+} ions and with holes in alkali and silver halides.

Spectroscopic Splitting Factor

We suppose for convenience that the crystal field constants, A, B are such that $U_x = xf(r)$ is the orbital wave function of the ground state of the atom in the crystal. For a spin $S = \frac{1}{2}$ there are two possible spin states $S_z = \pm\frac{1}{2}$ represented by the spin functions α, β , which in the absence of a magnetic field are degenerate in the zeroth approximation. The problem is to take into account the spin-orbit interaction energy $\lambda \mathbf{L} \cdot \mathbf{S}$.

If the ground state function is $\psi_0 = U_x \alpha = xf(r)\alpha$ in the zeroth approximation, then in the first approximation, considering the $\lambda \mathbf{L} \cdot \mathbf{S}$ interaction by standard perturbation theory, we have

$$\psi = [U_x - i(\lambda/2\Delta_1)U_y]\alpha - i(\lambda/2\Delta_2)U_z\beta, \quad (30)$$

where Δ_1 is the energy difference between the U_x and U_y states, and Δ_2 is the difference between the U_x and U_z states. The term in $U_z\beta$ actually has only a second-order effect on the result and may be discarded. The expectation value of the orbital angular momentum to the first order is given directly by

$$\langle \psi | L_z | \psi \rangle = -\lambda/\Delta_1,$$

and the magnetic moment of the state as measured in the z direction is

$$\mu_B \langle \psi | L_z + 2S_z | \psi \rangle = [-(\lambda/\Delta_1) + 1]\mu_B.$$

As the separation between the levels $S_z = \pm\frac{1}{2}$ in a field H is

$$\Delta E \approx g\mu_B H = 2[1 - (\lambda/\Delta_1)]\mu_B H,$$

the g value or spectroscopic splitting factor (12) in the z direction is

$$g = 2[1 - (\lambda/\Delta_1)]. \quad (31)$$

Van Vleck Temperature-Independent Paramagnetism

We consider an atomic or molecular system which has no magnetic moment in the ground state, by which we mean that the diagonal matrix element of the magnetic moment operator μ_z is zero.

Suppose that there is a nondiagonal matrix element $\langle s | \mu_z | 0 \rangle$ of the magnetic moment operator, connecting the ground state 0 with the excited state s of energy $\Delta = E_s - E_0$ above the ground state. Then by standard perturbation theory the wavefunction of the ground state in a weak field ($\mu_2 B \ll \Delta$) becomes

$$\psi'_0 = \psi_0 + (B/\Delta)\langle s | \mu_z | 0 \rangle \psi_s, \quad (32)$$

and the wavefunction of the excited state becomes

$$\psi'_s = \psi_s - (B/\Delta)\langle 0|\mu_z|s\rangle\psi_0 . \quad (33)$$

The perturbed ground state now has a moment

$$\langle 0'|\mu_z|0'\rangle \cong 2B|\langle s|\mu_z|0\rangle|^2/\Delta , \quad (34)$$

and the upper state has a moment

$$\langle s'|\mu_z|s'\rangle \cong -2B|\langle s|\mu_z|0\rangle|^2/\Delta . \quad (35)$$

There are two interesting cases to consider:

Case (a). $\Delta \ll k_B T$. The surplus population in the ground state over the excited state is approximately equal to $N\Delta/2k_B T$, so that the resultant magnetization is

$$M = \frac{2B|\langle s|\mu_z|0\rangle|^2}{\Delta} \cdot \frac{N\Delta}{2k_B T} , \quad (36)$$

which gives for the susceptibility

$$\chi = N|\langle s|\mu_z|0\rangle|^2/k_B T . \quad (37)$$

Here N is the number of molecules per unit volume. This contribution is of the usual Curie form, although the mechanism of magnetization here is by polarization of the states of the system, whereas with free spins the mechanism of magnetization is the redistribution of ions among the spin states. We note that the splitting Δ does not enter in (37).

Case (b). $\Delta \gg k_B T$. Here the population is nearly all in the ground state, so that

$$M = \frac{2NB|\langle s|\mu_z|0\rangle|^2}{\Delta} . \quad (38)$$

The susceptibility is

$$\chi = \frac{2N|\langle s|\mu_z|0\rangle|^2}{\Delta} , \quad (39)$$

independent of temperature. This type of contribution is known as Van Vleck paramagnetism.

COOLING BY ISENTROPIC DEMAGNETIZATION

The first method for attaining temperatures much below 1 K was that of isentropic, or adiabatic, demagnetization of a paramagnetic salt. By its use, temperatures of 10^{-3} K and lower have been reached. The method rests on the fact that at a fixed temperature the entropy of a system of magnetic moments is lowered by the application of a magnetic field.