Impurities in singlet magnets

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It is shown that doping of certain singlet magnets with small amounts of magnetic impurities alters radically the state of the magnetic system of the matrix. In particular, ferromagnetic order may be produced in substances that are paramagnetic in the absence of impurities even at zero temperature. The impurity-induced transition from the ferromagnetic state into the paramagnetic state is also considered.

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Rare-earth magnets such as Pr and Pr_3Tl, in which the ground state of the f level in the crystal field is a nonmagnetic singlet, are presently under intense study.[1–5] Magnetic order takes place in such systems only if the exchange interaction is strong enough. This interaction, by "mixing" the wave functions of the sublevels, then induces a moment in the system. Within the framework of the singlet-singlet model, in which the excited states are replaced by one singlet, the Hamiltonian of the considered magnets can be reduced to the Ising model with a transverse magnetic field[4]:

$$\mathcal{H} = -\Delta \sum_i S_i^z - \sum_{i,j} V(r_{ij}) S_i^x S_j^x .$$

Here **S** are pseudospin-$\frac{1}{2}$ operators acting on the wave functions of the sublevels, Δ is the difference of the sublevel energies, and $V(r)$ is proportional to the exchange integral.

Within the framework of the singlet-singlet model, the atom total-angular-momentum operators J_i are connected with S_i by the relation $J_i^x = J_i^y = 0$ and $J_i^z = \alpha S_i^x$ (α is a numerical coefficient). The molecular-field method makes ferromagnetism possible in such systems only if $\eta = V(k=0)/\Delta > 1$ ($V(k)$ is the Fourier transform of $V(r)$). At $\eta > 1$ we have $\langle J_i^z \rangle \approx \langle S_i^x \rangle = 0$ and the system is paramagnetic even at zero temperature $T=0$. A detailed analysis of the model described above is contained, e.g., in[3].

At present we know of a number of singlet magnets (Pr, Pr_3Tl, etc) for which $|\eta - 1| \ll 1$.[1,2] For example, for Pr_3Tl we have $\eta - 1 = 0.06$. In this paper it will be shown that by alloying these substances with small amounts of impurities it is possible to alter greatly the properties of the matrix, viz., to change it from the ferromagnetic to the paramagnetic state and vice versa, or to change the magnetization by several times.

We consider only impurities that do not change the crystal field at the matrix atoms. These properties are possessed by the rare-earth impurities used in[1,5]. The ground state of the f level of the impurity ion will be assumed to be magnetic (this is certainly the case if the total angular momentum I of the impurity is half-integer), so that the splitting of the f level of the impurity is immaterial to us. Using the connection between the operators J and S, the interaction Hamiltonians of such impurities with the matrix can be expressed in the form

$$\mathcal{H}_{imp} = -\sum_{i,j} U(r_i - r_j) S_i^x I_i^z.$$

We consider first the case of a paramagnet. In first-order perturbation theory in $U(k=0)/\Delta \ll 1$ ($U(k)$ is the Fourier transform of $U(r)$), we can obtain the following expression for the distribution of the magnetic moment of the matrix at a distance r from the impurity

$$M^z(r) = I^z a\mu_h \int U(k)\chi(k) e^{i\mathbf{kr}} \frac{d^3\mathbf{k}}{(2\pi)^3}.$$

Here μ_h is the magnetic moment of the matrix atom, and the function $\chi(k)$ differs from the susceptibility of the matrix only in the absence of the factor $(\mu_h)^2$. According to[3] we have at $T \ll \Delta\sqrt{1-\eta}$

$$\chi(k) = [\Delta - V(k)]^{-1}.$$

Expanding $V(k)$ in a series at small values of k, viz., $V(k) = V(0)[1 + k^2a^2]$, we obtain

$$M^z(r) = I^z a\mu_h \frac{U(0)}{4\pi\Delta a^2} \frac{1}{r} \exp\left(-\frac{r}{R}\right). \tag{1}$$

The quantity $R = a(1-\eta)^{-1/2}$ has here the meaning of the correlation radius of an ideal matrix near the point of the phase transition with respect to the parameter η. The effective magnetic moment μ_{eff} of the impurity is calculated by integrating (1), and turns out to be equal to

$$\mu_{eff} = \mu_i\left(1 + \frac{a\mu_h}{\mu_i} \frac{U(0)}{\Delta(1-\eta)}\right) \tag{2}$$

where μ_i is the magnetic moment of the impurity.

If the parameter of the coupling with the matrix $U(0)/\Delta$ is not too small then, as seen from (2), $\mu_{eff} \gg \mu_i$. The slow decrease of $M^z(r)$ and the presence of a "giant" effective moment of the impurities are due to the large value of the correlation radius near the point of the phase transition with respect to η.

The overlap of the polarization regions localized near the impurities leads to the appearance of an indirect exchange interaction of the impurity spins (it can also be treated as an indirect exchange of matrix paramagnons). The effective Hamiltonian of this interaction is of the form

$$\mathcal{H}_{eff} = -V_0 \sum_{ij} I_i^z I_j^z \frac{1}{r_{ij}} \exp\left(-\frac{r_{ij}}{R}\right),$$

where $V_0 = U^2(0)\Omega_e/4\pi\Delta a^2$, and Ω_0 is the volume of the unit cell. Since $V_0 > 0$, this interaction leads to the appearance of an impurity ferromagnetism with a saturation moment equal to $M = \mu_{eff}n$ (n is the impurity concentration). All the formulas derived above are valid only at low concentrations $c \ll 1-\eta$ ($c = n\Omega_0$), when the relative polarization of the matrix is small.

The thermodynamics of disordered ferromagnets with exponentially decreasing exchange potential was investigated in[6]. It is shown, in particular, that the Curie temperature T_C depends on the impurity concentration like

$$T_C \sim \exp(-0.89/n^{1/3}R),$$

and the temperature dependences of the magnetization and of the heat capacity have a number of anomalies in comparison with the usual relations that hold for spatially-ordered ferromagnets.

At $c \gtrsim 1-\eta$ the matrix is fully polarized. T_C and M depend on n more weakly than at low concentrations.

Introduction of nonmagnetic impurities into a singlet ferromagnet with $1 \gg \eta - 1 > 0$ leads to a decrease of the magnetization near the impurities, which decreases with distance in analogy with[1]. At $c \ll c_1 = \eta - 1$ the relative decrease of the saturation magnetization is $-\delta M/M = c/2c_1$. At $c = c_{cr} \sim c_1$, when $-\delta M = M$, the system becomes paramagnetic.

Introduction of magnetic impurities in the most realistic case $|U(0)/\Delta| \sim 1$ causes the magnetic moment of the matrix atoms to "unfreeze" at $c \gtrsim c_1$, and the magnetization increases by a factor $(\eta - 1)^{-1/2}$.

The vanishing of the magnetic order in singlet ferromagnets alloyed with nonmagnetic impurities was observed in[1,5]. Pr_3Tl becomes a paramagnet when 6–8% of La atoms are introduced.[1] This value of c_{cr} correlates well with the value 0.06 of c_1 of Pr_3Tl. Unfortunately, there are not enough data in[1] for a detailed comparison of theory with experiment.

To study the phenomena considered above it would be highly desirable to perform, besides macroscopic measurements, also experiments on elastic neutron scattering. It would then be possible to determine the distribution of the magnetization near the impurity from the peak of the forward scattering.

A study of singlet magnets with impurities would be useful, besides the possibility of significantly altering the properties of the matrix, for the determination of the parameters of singlet systems. This would be aided by the presence of rather unique concentration and temperature dependences.

The results remain qualitatively the same when the model is further refined, since they are connected only with the proximity to the point of the phase transition with respect to η.

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