STUDY OF WEAK EXCHANGE INTERACTION BY THE METHOD OF PARAMAGNETIC RESONANCE

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The EPR spectrum of exchange pairs in zinc fluorosilicate is studied experimentally and theoretically. Values of the exchange integral are obtained directly from the EPR spectrum for various types of pairs.

THERE have been recent studies of the EPR spectra of many exchange pairs [1], i.e. systems consisting of two paramagnetic ions, randomly located near each other, between which appreciable exchange forces act. The basic part of the interaction between the paramagnetic particles, which depends on their spins $\mathbf{S}_1$ and $\mathbf{S}_2$, has an isotropic character and is described by the Hamiltonian $\mathcal{H}_{ex} = J(\mathbf{S}_1 \cdot \mathbf{S}_2)$. In the substances investigated $J \gg \mathcal{H}_{sp}$ where $\mathcal{H}_{sp}$ denotes an interaction described by the spin Hamiltonian of an individual paramagnetic ion. Because of this condition the EPR spectrum does not furnish a direct measurement of J. The magnitude of the exchange interaction can be only approximately estimated from the temperature dependence of the intensity of the resonance line. If $J \approx \mathcal{H}_{sp}$, then the study of the EPR spectrum of exchange pairs can furnish a high precision method for determining J.

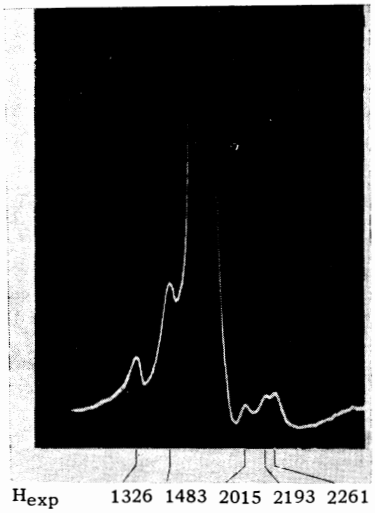
We have studied the EPR spectrum of Ni^{2+} exchange pairs formed in monocrystalline $ZnSiF_6 \cdot 6H_2O$, in which 2% of the zinc ions were isomorphously replaced by nickel. The measurements were made by means of a superheterodyne radiospectroscope at 9.4×10^9 cps and 1.5°K. We established, close to the two fundamental absorption peaks, the existence of a large number of less intense subsidiary peaks. These peaks can be assigned, according to the character of the angular dependence of the EPR spectrum, to three groups which correspond to three possible types of exchange pairs: 1) pairs with spacing $d_1 = 6.21$ Å between nickel ions oriented along the [1,0,0] axis, 2) pairs with spacing $d_2 = 1.33d_1$ and [1,1,0] orientation, and 3) pairs with spacing $d_3 = 1.48d_1$ and [1,1,0] orientation. The EPR spectra of all three types of pairs can be adequately interpreted with the help of the spin Hamiltonian:

$$\mathcal{H} = D(S_{z1}^2 + S_{z2}^2) + g\beta\mathbf{H}(\mathbf{S}_1 + \mathbf{S}_2) + J(\mathbf{S}_1\mathbf{S}_2), \quad (1)$$

where the constants D and g have the same values as for the fundamental EPR spectrum of the Ni ions. $J = -0.025 \pm 0.003$ cm^{-1} for pairs of the first type, $J = -0.014 \pm 0.003$ cm^{-1} for pairs of the second type and $J \approx -0.008$ cm^{-1} for pairs of the third type. It is clear that there exist other types of pairs, for example ions arranged on neighboring lattice sites along a [1,1,1] trigonal axis, however the exchange forces connecting them are so small that the spectrum of such pairs merges with the spectrum of the individual particles.

In the figure we show a photograph of the section of the EPR spectrum near the fundamental $-1 \longleftrightarrow 0$ absorption peak for the case $\mathbf{H} \parallel z$. The positions of the absorption peaks calculated from (1) with the help of selection rules and of those measured experimentally do not differ by more than 60 Oe. These differences are apparently due to magnetic dipole interactions and to unaccounted for anisotropic exchange forces. The already mentioned difference in the behavior of the EPR spectra of the different types of pairs under changes of crystal orientation is due to the influence of these interactions.

The case considered by us differs from earlier work on exchange pairs in the following respects: 1) $|J|$ is small, which evidently shows the absence of an indirect exchange interaction, 2) $J < 0$ (as for a ferromagnet), 3) pairs consist of ions with integral spin ($S = 1$), and therefore many pair resonance lines coincide with the lines of the individual ions. Our conclusions regarding $|J|$ agree with those Ollom and Van Vleck [2] drew from a study of experimental data on specific heat and the Faraday effect in nickel fluorosilicate. The estimate of $|J|$ made by Ishiguro et al [3] on



H_{exp}	1326	1483	2015	2193	2261
H_{theor}	1378	1540	1998	2197	2253
Pair type	1	2	2	1	1

Section of the EPR spectrum near the $-1 \leftrightarrow 0$ absorption line.

the basis of a calculation of exchange narrowing of the EPR lines also agrees with ours.

The existence of exchange pairs in $(Zn, Ni)SiF_6 \cdot 6H_2O$ can explain the experimentally established dependence of the spin-lattice relaxation time τ on the concentration of paramagnetic centers [4]. If it is assumed that the relaxation time τ_p is shorter for exchange pairs than for isolated ions, then the pairs will act as intermediaries between the ion spins and lattice vibrations in the relaxation process. It should be noted that in our case the spin-spin interactions will promote a particularly rapid transfer of energy from the individual ion spins to the pair spins, since many of the pair energy intervals coincide with the intervals between the Ni^{2+} spin levels. An estimate of τ_p made by the continuous saturation method showed that in fact $\tau_p < \tau$. The question of the nature of the spin-phonon interaction of pairs requires a special investigation. From [5] it follows that the modulation of the exchange interactions by the lattice vibrations cannot give the required values of τ_p. The strengthening of the spin-phonon interaction upon formation of pairs may be due to the lowered symmetry of the surrounding crystalline field and to the increased number of spin levels.

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62