averaged over the states on the Fermi surface; n is the number of electrons per unit cell of a nonmagnetic atom; ρ is the degree of polarization of these electrons; μ_B is the Bohr magneton. The measured isomeric shifts indicate that the electron density in the vicinity of an Sn nucleus is approximately the same in the cases discussed above. Moreover, the electron density decreases in all three systems under pressure. In accordance with Eq. (4), we would expect the absolute values of the fields to decrease in all cases, which is not in agreement with the experimental results. (We are allowing here for the fact that, in the range of pressures employed, the values of ρ also decrease proportionally to σ, whereas n remains practically constant.)

Thus, we may conclude that the dependences $H(P)$ can be explained if allowance is made for two contributions of opposite sign and with radial dependences. Moreover, the model of "competing contributions" explains qualitatively the experimental results. A fuller check of this model and its refinement would require new experimental data particularly on systems in which one of the contributions to the hyperfine field predominates over the other.

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Isotropic exchange interaction of pairs on Ni^{2+} ions in zinc fluorosilicate at high pressures

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The crystal resonator method was used in an ESR investigation of the dependences of the exchange integrals of Ni^{2+} ion pairs in $ZnSiF_6{\cdot}6H_2O$ single crystals on hydrostatic pressure. The investigation was carried out in the frequency ranges 24 and 72 GHz at temperatures of 1.6–4.2°K. A change in the isotropic exchange interaction was deduced from the high-pressure ESR spectra of exchange pairs recorded for various orientations of the magnetic field relative to the C_3 symmetry axis. The exchange integral of the nearest-neighbor Ni^{2+} ion pairs increased exponentially when the lattice constant was reduced by compression.

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1. INTRODUCTION

Investigation of the exchange interactions of impurity ion pairs in diamagnetic matrices provides one of the direct methods for the identification of the process of formation of exchange-coupled clusters in magnetic materials, determination of the magnetic structures of these clusters, and estimation of the adequacy of the description of local and macroscopic properties. Determination of the exchange integrals by the ESR method is now traditional. However, in the case of weakly coupled exchange pairs of Ni^{2+} ions in $ZnSiF_6 \cdot 6H_2O$[1] the ESR method has made it possible to determine spectroscopically the exchange integrals. Therefore, a high-pressure investigation of the ESR spectra of Ni^{2+} exchange pairs in $ZnSiF_6 \cdot 6H_2O$ provides an opportunity for direct determination of the dependences of the exchange integrals on the interionic distances.

The ESR spectrum of exchange pairs is described under normal conditions by the spin Hamiltonian[1]

$$\hat{\mathscr{H}} = g\beta\mathbf{H}(\mathbf{S}_1+\mathbf{S}_2) + D(S_{1z}^2+S_{2z}^2) + J(\mathbf{S}_1\mathbf{S}_2), \qquad (1)$$

where the spectroscopic splitting factor is isotropic and equal to $g = 2.230 \pm 0.005$, D is the initial splitting of nickel ions in the trigonal field, $D = -0.134 \mp 0.005\ \mathrm{cm}^{-1}$, and J is the exchange integral of the isotropic interaction.

If a magnetic field H_0 is oriented parallel to the symmetry axis C_3, the eigenvalues and wave functions of the Hamiltonian (1) are found by diagonalizing it (see, for example, [2]). Another convenient orientation for which we can diagonalize (1) is that in which a magnetic field H_0 makes an angle $\gamma = 54^\circ 44'$ relative to the symmetry axis C_3 (γ orientation). In this case, the trigonality parameter described by the second term in Eq. (1) is eliminated from the pair spectrum.[3] The spin Hamiltonian describing the spectrum of pairs under these conditions is

$$\mathcal{H}=g\beta\mathbf{H}(\mathbf{S}_1+\mathbf{S}_2)+J(\mathbf{S}_1\mathbf{S}_2). \tag{2}$$

The energy levels and energies of the allowed transitions are

$$\left.\begin{array}{l}\varepsilon_{1,9}=\mp 2g\beta H+J, \quad \varepsilon_{2,7}=\mp g\beta H-J,\\ \varepsilon_{3,8}=\mp g\beta H+J, \quad \varepsilon_4=-J, \quad \varepsilon_{5,6}=-J/2\pm 3J/2;\end{array}\right\} \tag{3}$$

$$\left.\begin{array}{l}\varepsilon_1-\varepsilon_3=\varepsilon_2-\varepsilon_4=-g\beta H, \quad \varepsilon_3-\varepsilon_5=\varepsilon_4-\varepsilon_7=-g\beta H,\\ \varepsilon_5-\varepsilon_8=\varepsilon_7-\varepsilon_9=-g\beta H, \quad \varepsilon_3-\varepsilon_6=3J-g\beta H, \quad \varepsilon_6-\varepsilon_8=-3J-g\beta H.\end{array}\right\} \tag{4}$$

We can see that all the transitions in the spin system of pairs are identical, with the exception of the transitions $\varepsilon_3 \leftrightarrow \varepsilon_6$ and $\varepsilon_6 \leftrightarrow \varepsilon_8$. The parameter J can be found directly from the difference between the positions of two lines in a spectrum. The expression for the energies of the $\varepsilon_3 \leftrightarrow \varepsilon_6$ and $\varepsilon_6 \leftrightarrow \varepsilon_8$ transitions gives

$$J={}^1/_6 g\beta(H_{3-6}-H_{6-8}).$$

where H_{3-6} is the resonance value of the magnetic field corresponding to a microwave transition ($h\nu$) between the energy levels ε_3 and ε_6; H_{6-8} is the corresponding value for the transition between the levels ε_6 and ε_8.

Measurements of the pair spectra at normal pressure and $T = 4.2$ °K in the orientations $H_0 \parallel C_3$ and $H_0 \perp C_3$ indicate that the exchange integral of a pair of nearest-neighbor ions is the same (within the limits of experimental error) for both orientations and amounts to $J_1 = -0.0303 \pm 0.0005$ cm^{-1}. This agreement between the exchange integrals is additional evidence of the isotropy of the interaction. This isotropy was monitored continuously in the high-pressure measurements.

2. CRYSTAL STRUCTURE. COMPRESSIBILITY

Pauling established[4] that fluorosilicates are isomorphous with $NiSnCl_6 \cdot 6H_2O$ and represent double-complex compounds $[Me \cdot (H_2O)_6][SiF_6]$. They crystallize in a trigonally distorted structure of the CsCl type with the space group $C_{3i}^2(R\bar{3})$. The distortions are due to compression along the trigonal axis which alters the rhombohedral angle to $\alpha = 96^\circ 6'$ and the rhombohedral unit cell parameter of $ZnSiF_6 \cdot 6H_2O$, given by Wyckoff,[5] is $d_0 = 6.297$ Å (298 °K).

Measurements of the elastic moduli$^{1)}$ were used to estimate the compressibility parallel and perpendicular to the trigonal axis at $T = 298$ °K:

$$\left.\begin{array}{l}(\partial \ln l\ /\partial P)_{P=0}=-(1.4\pm0.1)\cdot 10^{-6}\ \text{bar}^{-1},\\ (\partial \ln l_\perp/\partial P)_{P=0}=-(3.5\pm0.2)\cdot 10^{-6}\ \text{bar}^{-1}.\end{array}\right\} \tag{5}$$

The observed compressibility anisotropy yielded the following important conclusion: at high pressures, the rhombohedral angle α tended to 90°, i.e., the symmetry of the unit cell changed under pressure from trigonal to cubic.

3. HIGH-PRESSURE MEASUREMENTS

The exchange pair spectra were determined using superheterodyne ESR spectrometers at frequencies of 24, 37, and 75 GHz in the temperature range 1.6–4.2 °K by the crystal resonator method in a high-pressure chamber with a waveguide input of microwave power. Cylindrical samples, 7.0 mm in diameter and 12.0 mm long (crystal resonators tuned to the H_{012} mode at a working frequency of 24 GHz), were made from $ZnSiF_6 \cdot 6H_2O$ single crystals with Ni^{2+} concentrations from 0.1 to 5%. The Q factor of the crystal resonators, placed inside thin-walled copper cylinders under pressure at helium temperatures, was of the order of 10^3. The method made it possible to measure the pair lines of very low intensity at high pressures by display on the screen of an oscillograph.

Throughout the investigated temperature range from 300 to 1.6 °K the high pressures were measured with a calibrated manganin manometer. Room-temperature calibration with a secondary standard from the All-Union Scientific-Research Institute of Physicotechnical and Radio Engineering Measurements was supplemented by low-temperature calibration based on the superconducting transition in In, which was accurate to 0.2 kbar.

Residual broadening of single ESR fine-structure lines of Ni^{2+} was observed at low temperatures and this broadening depended strongly on the conditions during the application of high pressures and subsequent cooling to helium temperatures. This line broadening reflected the sensitivity of the non-Kramers Ni^{2+} ion to the inhomogeneity of the internal crystal field. When the pressure-transmitting medium was an oil–kerosene mixture, the rate of the rise in pressure was not more than 1 kbar/h, and the rate of cooling did not exceed 30 deg/h, the residual broadening of the ESR lines of a sample of $ZnSiF_6 \cdot 6H_2O$ with 1% Ni^{2+} did not exceed 30 G. Since the rate of change in the initial splitting D of the Ni^{2+} ions at low pressures was 860 G/kbar, the pressure inhomogeneity did not exceed 40 bar, which represented less than 1% for pressures above 4 kbar.

These estimates indicated that the ESR spectra of the Ni^{2+} ion pairs in $ZnSiF_6 \cdot 6H_2O$ were determined at high pressures under homogeneous hydrostatic conditions and the lattice symmetry was maintained or even improved. The changes in the unit cell parameters were a reduction in the lattice constant and in the angle α. According to Eq. (5), the linear compressibility term was

$$(\partial \ln d_0/\partial P)_{P=0}=-(2.8\pm0.2)\cdot 10^{-6}\ \text{kbar}^{-1}.$$

4. RESULTS

Measurements of the ESR spectra of Ni^{2+} ions in $ZnSiF_6 \cdot 7H_2O$, carried out under hydrostatic compression conditions up to 12 kbar at helium temperatures in the $H_0 \parallel C_3$ orientation, and of the angular dependence in the $H_0 \parallel C_3$ and $H_0 \perp C_3$ planes, established that the behavior of the spin triplet at high pressures was described by the axial spin Hamiltonian

$$\mathcal{H}=g\beta HS_z+D(S_z^2-{}^2/_3), \tag{6}$$

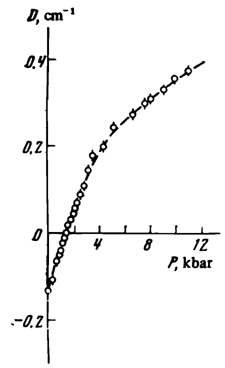

FIG. 1. Dependence of the initial splitting of the ground state of the Ni^{2+} ions in $ZnSiF_6 \cdot 6H_2O$ on hydrostatic pressure.

where $g = 2.23 \pm 0.01$ was isotropic and independent of pressure, whereas the parameter D was a function of pressure (Fig. 1).

Throughout the investigated range of pressures, the weaker absorption line was resolved near a fine-structure doublet. The number of such lines, their relative intensities for samples with impurity concentrations ranging from 0.1 to 5% Ni^{2+}, and the nature of the angular dependences near $H_0 \parallel C_3$ and $H_0 \perp C_3$ indicated that all the absorption lines in the pair spectra could be divided into three groups corresponding to three possible types of exchange-coupled pairs identified under normal pressures.[2]

An investigation of the ESR spectra of pairs at three very different frequencies of 24.4, 35, and 75 GHz gave results which agreed within the experimental error, demonstrating the correctness of the selected transitions between the energy levels of the exchange-coupled pairs.

Figure 2 shows the positions of all the lines in the pair spectra recorded in a magnetic field at 23.9 GHz as a function of pressure in the case when H_0 was parallel to the C_3 symmetry axis. Throughout the investigated range of pressures, the spectra of the exchange pairs were described by the Hamiltonian (1). The characteristics of pairs of different signs were not affected when the sign of the trigonal field was reversed. For example, the center of gravity of lines in the first pair of $D < 0$ was shifted (relative to the lines of isolated ions) to the overall center of symmetry of the spectrum, as shown in Fig. 2; a reversal of the sign of $D > 0$ shifted the center of gravity in the opposite direction, which corresponded to energy levels of exchange pairs with the reverse sign of D.

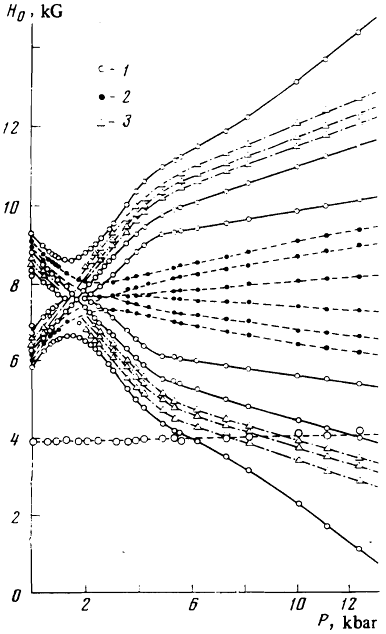

FIG. 2. Influence of hydrostatic pressure on the positions of resonance lines of the pair spectra of the Ni^{2+} ions in a magnetic field parallel to the symmetry axis C_3.

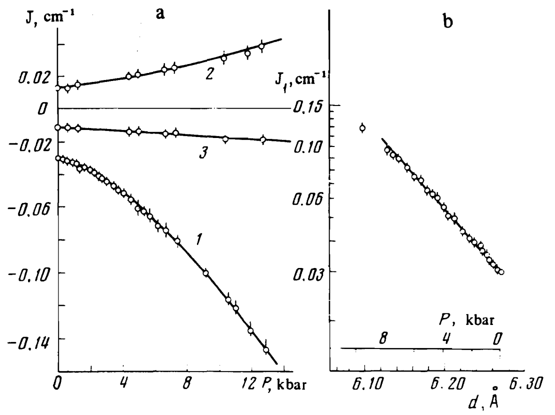

FIG. 3. a) Dependence of the exchange integrals of three types of the Ni^{2+} ion pair in $ZnSiF_6 \cdot 6H_2O$ on hydrostatic pressure: 1) integral J_1 for the nearest-neighbor ions; 2), 3) integrals J_2 and J_3 for more distant coordination spheres. b) Dependence of the exchange integral of the nearest-neighbor ions J_1 on the lattice parameter d. The energy is plotted on a logarithmic scale.

Changes in the exchange integrals of the first three coordination spheres are illustrated in Fig. 3.[2)] Throughout the investigated range of pressures, the measurements in the $H_0 \parallel \gamma$ orientation of the exchange integral J_1 agreed, within the limits of the experimental error (up to 2%), with the values measured in the $H_0 \parallel C_3$ orientation, which was typical of the isotropic exchange interaction.

5. INFLUENCE OF DEUTERATION

The ESR spectrum of exchange pairs of nickel was determined for $ZnSiF_6 \cdot 6D_2O$ with 1% Ni^{2+}. As in the case of hydrated crystals, the exchange interactions were relatively weak and the exchange pair lines were grouped around two main absorption lines of isolated ions, partly overlapping these lines and one another. Figure 4 shows the spectrum obtained in the $H_0 \parallel C_3$ orientation. The spectrum was symmetric relative to $H_0 = 7675$ G (frequency $\nu = 23.92$ GHz), corresponding to the g factor of a single ion $g = 2.23 \pm 0.01$. Since the center of gravity of the group of lines 1–8 was shifted relative to the lines of isolated ions toward the overall center of symmetry of the spectrum, we concluded that the ions in a pair were coupled by the ferromagnetic interaction: $J < 0$. This conclusion also followed from the temperature dependence of the relative intensities

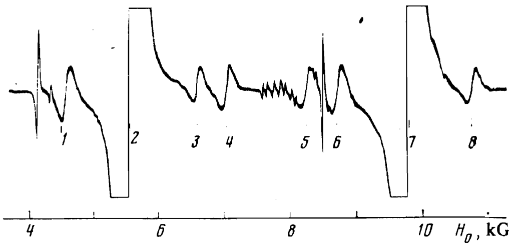

FIG. 4. Derivative of the absorption spectrum of $ZnSiF_6 \cdot 6D_2O$ with 1% Ni^{2+} recorded in a magnetic field parallel to the C_3 symmetry axis at 25.2 GHz and $T = 4.2\,°K$. The numbers 1–8 denote the lines belonging to the exchange pair of nearest-neighbor ions.

of the lines in the pair spectrum. The exchange integrals deduced from Eqs. (1) and (2) were both $J_1 = -0.069 \pm 0.002\ \mathrm{cm}^{-1}$. The spectrum of the exchange pairs included lines due to pairs with a weaker interaction but the line broadening made it impossible to obtain quantitative estimates of these interactions.

6. DISCUSSION

It is clear from Fig. 3 that the errors in the determination of the exchange integrals amounted to a few percent, whereas the actual values changed by hundreds of percent. This made it possible to establish that the pressure dependence of the integrals is essentially nonlinear. If the energy of the exchange integrals is plotted on a logarithmic scale (Fig. 3b), the dependence on the compression becomes linear. Consequently, the nearest-neighbor ions are characterized by an exponential dependence of the exchange integrals on the compression or on the interionic distances, which can be expressed analytically in the form[7]

$$J_1 = J_{10} \exp[-K(r - r_0)/r_0]; \tag{7}$$

here, the parameters J_{10} and r_0 are the values under normal conditions, and $K = 47 \pm 5$. The increase in the exchange integral due to the change in the volume V can be expressed in the form:

$$\partial \ln J_1 / \partial \ln V = -12 \pm 2.$$

This increase in the exchange integrals on compression makes it possible to carry out more detailed estimates of the correction Θ in the Curie–Weiss law for the concentrated salt $NiSiF_6 \cdot 6H_2O$. In the case of nickel fluorosilicate, the lattice constant is less than for $ZnSiF_6 \cdot 6H_2O$ and amounts to $d = 6.259$ Å and the difference by 0.038 Å corresponds to compression of $ZnSiF_6 \cdot 6H_2O$ by a pressure which can be found from the condition

$$P\left(\frac{\partial \ln d_0}{\partial P}\right) d_0 = 0.038\,\text{Å}: \qquad P = 2.0\ \text{kbar}.$$

Consequently, in the case of $ZnSiF_6 \cdot 6H_2O$ subjected to a pressure of 2.0 kbar, the distances between the Ni^{2+} impurity ions are approximately equal to the distances in nickel fluorosilicate. Then, the correction Θ is

$$\Theta = -\frac{S(S+1)}{3k} \sum_{i=1}^{i=3} Z_i J_i = \frac{2 \cdot 31.8 \cdot 10^{-18}}{3 \cdot 1.38 \cdot 10^{-16}} = +0.154 \pm 0.005\,°\text{K}.$$

According to Ohtsubo,[8] the Curie temperature of nickel fluorosillicate is $T_c = 0.150\,°K$, which is in agreement—within the limits of experimental error—with $\Theta = 0.154 \pm 0.005\,°K$.

The following conclusions can be drawn from the results reported above:

1) the dependence of the exchange integrals of the Ni^{2+} ions on the interatomic distances is exponential;

2) the exchange interaction in a pair of ions in a magnetically dilute crystal is identical, other conditions being constant, with the exchange interaction in magnetically concentrated systems (this result is valid for a weak exchange interaction when the exchange via a paramagnetic ion, i.e., via $2d_0$ and $3d_0$, is negligible).

We are grateful to K. S. Aleksandrov for acquainting us with the results of measurements of the elastic moduli of zinc fluorosilicate, and to S. N. Lukin and O. P. Tesla for their help in the measurements.

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[1] The elastic moduli were measured at the Laboratory of Crystal Physics of the Kirenskiĭ Institute of Physics, Siberian Branch, USSR Academy of Sciences, Krasnoyarsk, and the following values were obtained (in units of 10^{10} dyn/cm²): $c_{11} = 18.79 \pm 0.1$, $c_{33} = 38.97 \pm 0.1$, $c_{44} = 5.54 \pm 0.1$, $c_{66} = 5.76 \pm 0.1$, $c_{13} = 6.78 \pm 0.7$, $c_{14} = -1.37 \pm 0.1$, and $c_{25} = -0.15 \pm 0.02$.

[2] The lattice constant d in Fig. 3b at zero pressure was taken to be 6.273 Å ($T = 4.2\,°K$) instead of 6.297 Å ($T = 298\,°K$). This was due to the fact that we allowed for the correction $\Delta d_T = 0.024$ Å, due to the thermal expansion in accordance with the results of Walsh.[6]

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