

# Dependence of exchange integral on the hydrostatic pressure in a ferroelectric with hydrogen bonds

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We report observation, for the first time ever, of a decrease of the Heisenberg exchange when hydrostatic pressure is applied to a crystal.

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We present here the results of an EPR investigations of strong (up to  $10 \times 10^3$  kgf/cm<sup>2</sup>) hydrostatic pressure on the Heisenberg exchange integral  $J$  for impurity pairs Cr(III) in the lattice of the ferroelectric guanidine aluminum sulfate hexahydrate (GAS). Preliminary results were reported in<sup>[1]</sup>. Grooves in planes parallel to the  $C_3$  axis were cut on a GAS single crystal in the form of a right hexagonal prism.<sup>[2]</sup> The crystal was then placed in the slow-wave helix of a resonator of a special attachment, which was mounted in the EPR spectrometer.<sup>[3]</sup> Rotation of the helix in an external magnetic field  $H$  has made possible a sufficiently accurate orientation of the axis  $C_3 \parallel H$ . For this case, according to<sup>[4]</sup>, we carried out a subsequent reduction of the experiments, and the results of the reduction are shown in Fig. 1. An unexpected singularity, heretofore unobserved, was that when crystal compression force  $P$  is increased the exchange integral decreases,  $\partial J / \partial P < 0$ . (The exchange in the GAS is of antiferromagnetic origin).<sup>[4]</sup> A similar effect was observed also for the gallium isomer and for deuterated samples. We recall that in an earlier report<sup>[5]</sup> of the effect of hydrostatic pressure on the exchange integral between Ni(II) ions in a zinc fluorosilicate lattice it was stated that  $\partial J / \partial P > 0$  both for  $J > 0$  and  $J < 0$ .)

To understand our results, we start from the following premises. An investigation of the exchange parameter  $J$  of a number of isomorphous GAS crystals has shown that superexchange is effected via bridges that include the H bond, and the energy of this bond influences the transport of the spin density from one paramagnetic center Cr(III) to another.<sup>[4,6]</sup> The hydrostatic pressure, by deforming the lattice, brings the atoms closer together. Naturally, the distance between the oxygen atoms  $O \dots O$  in the H bonds should also decrease,  $R_{O \dots O} = 2.65 \text{ \AA}$ .<sup>[2]</sup> This displacement, in accordance with<sup>[7]</sup>, is accompanied by dilatation of the OH bond of the water of crystallization and causes the distance between the central positions in the two-minimum potential of the H bond to decrease. Thus, with increasing pressure, the proton tunneling increases and consequently the ordering of the H bond is disturbed. The latter, leading to a change of the bridge, decreases the exchange parameter. We note also two other factors whose action enhances the disordering of the H bond. These are the strong anisotropy of the isothermal compression of the GAS crystal,  $\partial e_{zz} / \partial e_{xx} \approx 50$ ,<sup>[8]</sup> and energy effects that lead to a larger distortion (flexure) of the H bond than of the valence angles of the water molecule.<sup>[9]</sup>

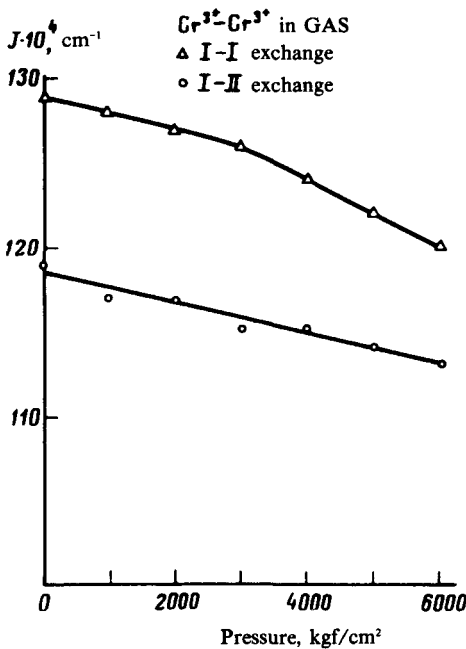


FIG. 1. Dependence of the exchange integral on the pressure. The symbols "I" and "II" stand for ions with point symmetry  $C_3$  and point symmetry  $C_{3v}$ , respectively.<sup>[2]</sup>

It has been noted that in the pressure range  $(7-8) \times 10^3$  kgf/cm<sup>2</sup> the resonant absorption is accompanied by a noticeable increase of the dielectric losses in the crystal. The error in the estimate of  $J$  is then worse than  $\pm 0.0002$  cm<sup>-1</sup>, and the corresponding results are not shown in Fig. 1. From experiments on the baric and thermal dependences  $J=f(P)$  and  $J=f(T)$ ,<sup>[1]</sup> and also from the data on the compressibility and thermal expansion of the GAS,<sup>[8]</sup> it follows that the change of  $|J|$  observed when the crystal is heated is almost four times larger than the change  $|J|$  due to the crystal deformation. When the foregoing functional dependences of  $J$  on the external actions are compared with the results of analogous experiments for the polarization vector  $\mathbf{P}_s$  in the GAS crystal,<sup>[10]</sup> it is seen that the energy of the thermal action on the parameters characterizing definite physical properties of the ferroelectric GAS is more effective than the baric action.

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<sup>1</sup>O.F. Gataullin, M.M. Saripov, and Yu. M. Ryzhmanov, Beiträge der Tagung HF Spektrome und ihre Anwendung, pp. 1-4, Leipzig, 1975.

<sup>2</sup>B.J.B. Schein and E.C. Lingafelter, J. Chem. Phys. **47**, 5183, 5190 (1967).

<sup>3</sup>A.I. Filippov, Prib. Tekh. Eksp. No. 5, 249 (1975).

<sup>4</sup>O.F. Gataullin, M.M. Zaripov, and Yu. M. Ryzhmanov, Fiz. Tverd. Tela (Leningrad) **16**, 2070 (1974) [Sov. Phys. Solid State **16**, 1344 (1975)].

<sup>5</sup>A.A. Galkin, A. Yu. Kozhukhar', and G.A. Tsintsadze, Zh. Eksp. Teor. Fiz. **70**, 248 (1976) [Sov. Phys. JETP **43**, 128 (1976)]; A. Yu. Kozhuhar and G.A. Tsintsadze, Phys. Lett. **55**, 175 (1975).

<sup>6</sup>O.F. Gataullin, M.M. Zaripov, and Yu. M. Ryzhmanov, Fiz. Tverd. Tela (Leningrad) **19**, 83 (1977) [Sov. Phys. Solid State **19**, 47 (1977)].

<sup>7</sup>A.R. Ubbelohde and K.J. Gallagher, Acta Crystallogr. **8**, 719 (1955).

<sup>8</sup>K.S. Aleksandrov and T.V. Ryzhova, *Kristallografiya* **6**, 289 (1961) [*Sov. Phys. Crystallogr.* **6**, 228 (1961)].

<sup>9</sup>N.D. Damm and R.P. Ozerov, *Kristallografiya* **17**, 437 (1972) [*Sov. Phys. Crystallogr.* **17**, 280 (1972)].

<sup>10</sup>J. Klimowski, K. Holdorna, R. Makawski, and D. Ozgo, *UAM Fiz. No.* **6**, 19 (1972).

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