

EPR STUDY OF THE $\text{KMgF}_3:\text{Ni}^{++}$ SINGLE CRYSTAL

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The EPR measurement of the magnetic Ni^{++} ion in KMgF_3 is presented. The values of the electronic g factor, the spin-orbit coupling constant λ and the effective magnetic moment μ_{eff} equal 2.2865, $-332.6232 \text{ cm}^{-1}$ and $3.2336 \mu_B$ respectively. The Lorentzian shape of the EPR line was determined by the least squares method. The comparison of the experimental results with the crystalline field and LCAO MO theories is discussed.

1. Introduction

The details of the EPR spectrum analysis for the octahedral $[\text{NiF}_6]^{4-}$ complex in the $\text{KMgF}_3:\text{Ni}^{++}$ (1%) single crystal and the comparison of the results with the calculations of the crystalline field and the LCAO MO (Linear Combination of Atomic Orbitals, Molecular Orbitals) theories are presented in this paper. The line shape, electronic g factor, the coupling constant λ of the spin-orbit operator $\lambda\vec{L}\vec{S}$, and the effective magnetic moment $\vec{\mu}_{\text{eff}}$ were determined.

The $\text{KMgF}_3:\text{Ni}^{++}$ one-dimensional antiferromagnet has a cubic perovskite structure in which the paramagnetic Ni^{++} ion is surrounded by a regular octahedron of fluorine ions with a point symmetry O_h [1, 2], (Fig. 1).

Recent EPR measurements in the $\text{KMgF}_3:\text{Ni}^{++}$ (1%) single crystal performed for temperatures of 20 K and 77 K have been related in the papers [6-8]. A broad line with superimposed sharp double quantum lines was observed. The electronic g factor due to the $\Delta M = \pm 1$ transitions was estimated as equal to 2.2797. The EPR spectrum was also investigated in a crystal of KMgF_3 containing 2% Ni^{++} , where no fluorine hfs was seen but weak broad lines were observed due to exchange coupled pairs of Ni^{++} ions.

Interesting results of the spin-phonon interaction of Ni^{++} ion pairs in KMgF_3 , studied by the acoustic paramagnetic resonance (APR) technique, have been presented in the paper [5]. The APR spectrum consists of intense lines caused by the $\Delta M = \pm 1$ transitions. The electronic g factor were evaluated as $g(\Delta M = 1) = 2.28$. The advantage of the APR

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measurement over the simpler EPR technique is that the acoustic selection rules allow the observation not only of the $\Delta M = 1$ transition, as in EPR, but also of ones in which $\Delta M = 2$. Hence resonance lines may often be observed by APR which are very small, or even undetectable in EPR experiment.

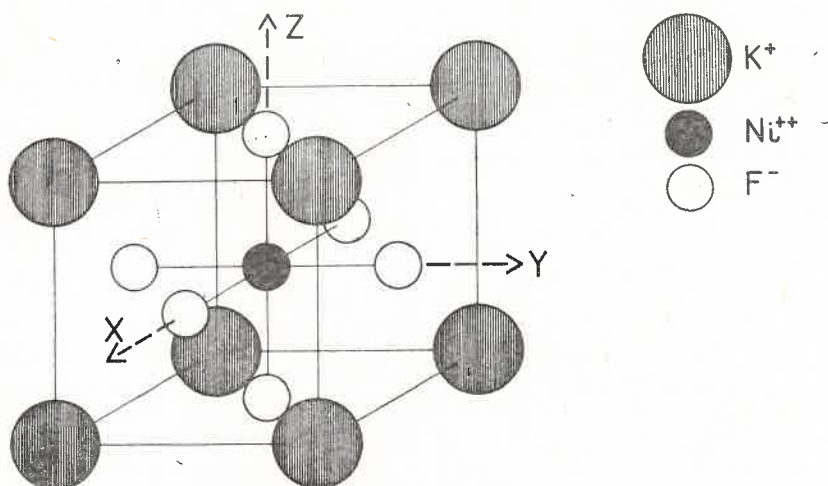


Fig. 1. Cubic perovskite structure of $\text{KMgF}_3:\text{Ni}^{2+}$ (lattice constant $a = 3.98717 \text{ \AA}$, distance $\text{Ni}^{2+}-\text{F}^- = 1.994 \text{ \AA}$)

2. Analysis of experimental results and discussion

The microwave EPR spectrometer SEX/28 with field modulation at a frequency of 100 kHz was used in this experiment. Measurements were made on the iron-group ion Ni^{2+} on magnesium lattice sites in the KMgF_3 single crystal at a frequency of 9.38 GHz

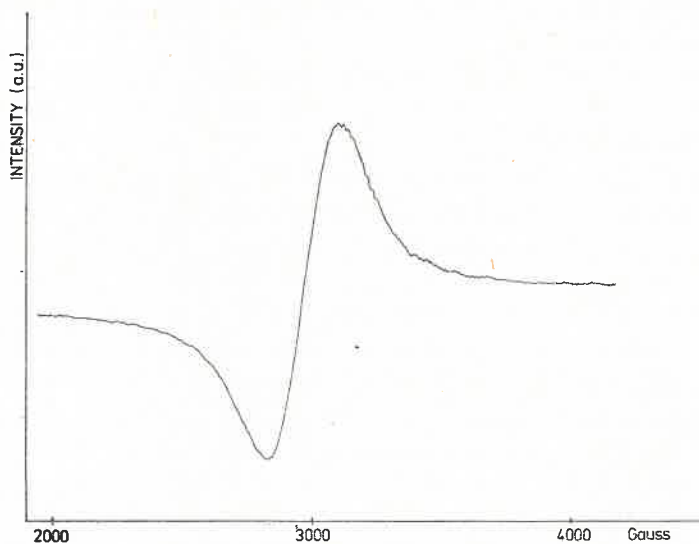


Fig. 2. The EPR spectrum of Ni^{2+} ion in KMgF_3

and at room temperature. The EPR spectrum was recorded in the first derivative absorption line (Fig. 2).

This spectrum is composed of one symmetrical and broad line at the resonant field H_{res}

$$H_{res} = hv/(g\mu_B) = 3079.6328 \text{ Gs.} \quad (1)$$

The small deviation from the line symmetry is due to the inaccuracy of the spectrometer. The value of g , related to the inhomogeneously broadened $\Delta M = \pm 1$ transitions, was estimated from the last equation as 2.2865. In the EPR spectrum no fluorine hfs or lines due to the forbidden $\Delta M = \pm 2$ transitions were observed; it is therefore possible to describe this spectrum by the spin Hamiltonian (2).

In the case of the octahedral $[\text{NiF}_6]^{4-}$ complex, the ground state of Ni^{++} ion [3, 6, 8] is $3d^8 {}^3F_4 (S = 1, L = 3)$. In an octahedral-cubic crystalline environment the orbital degeneracy of the F level of the ion is raised, giving a singlet ground state $\Gamma_2 ({}^3A_{2g})$ and two

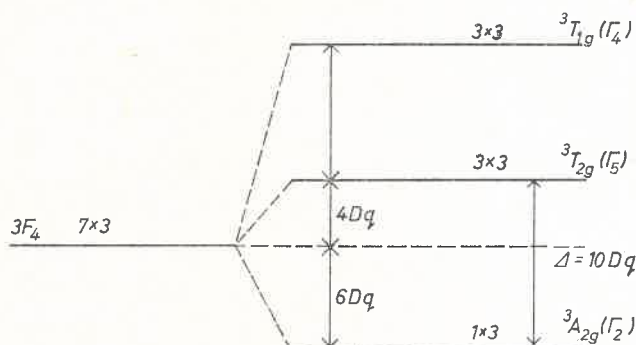


Fig. 3. The orbital and spin degeneracy of the F level in an octahedral-cubic crystalline field

excited triplets $\Gamma_5 ({}^3T_{2g})$ and $\Gamma_4 ({}^3T_{1g})$ (Fig. 3). In our case, the energetic distance $\Delta = 10 Dq$ between the ground state and the ${}^3T_{2g}$ level was obtained from the optical absorption spectrum, and equals 7250 cm^{-1} . This was evaluated [8] from the LCAO MO theory as equal to 6350 cm^{-1} . The magnetic moment related to the ${}^3A_{2g}$ state, for which the g factor is 2.0023 is of purely spin origin. The expected quantity of the orbital magnetic moment is described by

$$\vec{\mu} = \mu_B/\hbar \bar{L} = \mu_B/\hbar \langle \psi | \hat{L} | \psi \rangle, \quad (2)$$

where \hat{L} is the momentum. The condition necessary for non-vanishing integral is that the $\psi \hat{L} \psi$ function should contain a fully symmetrical symmetry group representation. From the symmetry group theory it follows that in the case of the octahedral complex (O_h) this condition is fulfilled by the T_1 and T_2 representations and not by A_2 . This leads us to the conclusion that the orbital magnetic moment due to the A state is completely quenched and contributes to the T_1 and T_2 states. The effective magnetic moment of the A state is determined by

$$\mu_{eff} = \mu_B g \sqrt{S(S+1)}, \quad (3)$$

where $g = g_0 = 2.0023$ in the first approximation. The spin-orbit coupling admixes the ground state ${}^3A_{2g}$ into the excited state ${}^3T_{2g}$ which is spin and orbitally degenerate. Consequently, the value of the spectroscopic splitting g factor is intermediate between the g values of these two mixing states; then the EPR spectrum should consist of a single line with g

$$g = 2(g_0 - \alpha\lambda/\Delta), \quad (4)$$

where g_0 is the free electron g value, λ is the spin-orbit coupling constant in solid and $\alpha = 2$ for Ni^{++} in KMgF_3 . This equation was derived [3] from the crystalline field theory; it gives us the value of the g factor as 2.2176. It has been shown in [8] that for the our case of Ni^{++} in the O_h symmetry, the electronic g factor should be expressed by the LCAO MO theory formula

$$g = 2.0023 - (8\lambda k_{\sigma\pi}^2/\Delta), \quad (5)$$

where λ is equal -320 cm^{-1} and $k_{\sigma\pi}$ is the orbital reduction factor (for the Ni^{++} ion in the O_h point symmetry $k_{\sigma\pi} = 0.88$), Δ is the distance between the ${}^3T_{2g}$ and ${}^3A_{2g}$ levels. This last term gives us the g factor value of 2.2734 ($\Delta = 7250 \text{ cm}^{-1}$ [8]) which agrees well enough with the experimental value for $g = 2.2865$, as opposed to the crystalline field theory results (see Eq. (8)). The difference $\Delta g = g - g_0 = +0.2842$ manifests the considerably large spin-orbit coupling effect on the EPR spectrum.

Using the experimental g value, the spin-orbit coupling constant $\lambda_{\text{exp}} = -332.6232 \text{ cm}^{-1}$ has been evaluated from Eq. (9), while $\lambda = -519.3353 \text{ cm}^{-1}$ has been found from Eq. (8). The large difference between experimental results and the crystalline field theory, and the agreement of the experimental data with the LCAO MO theory are understandable, since the crystalline field theory reduces the role of the ligand to the crystalline field production, which leads to energetic splitting of suitable central atom orbitals. The metal-ligand bonding has a purely electrostatic character here in the sense that its source is the electrostatic interaction of the transition element core plus its d electrons with the dipoles and charges surrounding this core. According to this theory, the electron probability clouds of the d -core complexes are not penetrating into the ligand electrons probability clouds, which often contradicted the experimental results. It is necessary to take into account at least a possibility of the reciprocal penetration of the probability clouds, as is the case in the LCAO MO theory.

A detailed presentation of this theory and its application in octahedral complexes can be found in the papers [3, 8, 14, 15].

The effective magnetic moment $\mu_{\text{eff}} = 3.2336 \mu_B$ has been calculated on the basis of expression (7), while the pure-spin moment μ_{eff}^0 is equal to $2.8317 \mu_B$. The difference $\Delta\mu_{\text{eff}} = \mu_{\text{eff}}(\text{exp}) - \mu_{\text{eff}}^0 = 0.4019 \mu_B$ is another evidence for the spin-orbit coupling. It is this coupling which leads to the admixture of the T_2 and A_2 states.

The EPR line shape has been determined by the least squares method [16] as Lorentzian. Its width at half maximum intensity was estimated as ~ 450 Gauss. This manifests the domination of the exchange interactions between the nearest electron spins over the spin-orbit coupling.

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