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Jahn-Teller Effect in Copper-Doped Spinel Group

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Abstract. Anomalous magnetic properties and various phase transitions observed in some spinels are due to the Jahn-Teller effect. The effect is rather effectively studied in corresponding diamagnetic analogues of such crystals. In the present paper a group of single crystals of normal and converted spinels doped with the two-valent copper Cu$^{2+}$ has been investigated. In this group of spinels the effect of inversion splitting shows itself classically. The investigations have been done by using radiospectrometers of 10 and 37 GHz frequency in the temperature range 4-300 K. For the first time, in the low-frequency range at the frequency of 10 GHz the full complex of the EPR spectra have been registered which are due to the theory of the inversion splitting. It consists of five types of the EPR spectra which are due to allowed $3^-\rightarrow 3^+$, $2^-\rightarrow 2^+$, $1^-\rightarrow 1^+$ and forbidden $3^-\rightarrow 1^+$, $1^+\rightarrow 2^-$ transitions. At passing to a higher frequency of 37 GHz there occurs the frequency transformation of the spectrum, the two EPR spectra are observed which have been observed by many authors in copper complexes in the case of Jahn-Teller effect developing.

1. INTRODUCTION

At present have been developed the general situation of the model of the Jahn-Teller effect. A large quantity of the experiment works has been performed. But it is not clear in the explanation and understanding of the appearance of the Jahn-Teller effect in the EPR spectra. It is necessary to find such an object of the investigations in which the Jahn-Teller effect appears in full. In this paper we study the octahedral copper complex. The ion Cu$^{2+}$ is situated in the oxygen octahedron. The ground state of the Cu$^{2+}$ ion (3d$^9$) in an octahedral field has a low-lying orbital doublet E. The low-lying level is orbital singlet which has the $|x^2-y^2>$ wave function. The Jahn-Teller effect is maximum for the D-ions. And such dg -electrons make the large Jahn-Teller distortions. Therefore we have the maximum effect for the Cu$^{2+}$-complex (3d$^9$). And the possibility of the appearance of the Jahn-Teller effect depends on the value of the inner asymmetry of the complex. The phenomenon of the inner asymmetry can take place in the case of the nonequivalent replacement. For example this is the case of replacement of the ion Li$^+$ by the ion Cu$^{2+}$ in LiGa$_2$O$_4$. In the spinel a ion Cu$^{2+}$ is compelled to displace from the center of the cation node. Such position of the Cu$^{2+}$ has provided a clear appearance of Jahn-Teller effect [1] in Li-spinels. In other matrices for example ZnAl$_2$O$_4$ and MgAl$_2$O$_4$ the appearance of the Jahn-Teller effect is very small. Because the Cu$^{2+}$-ions have replaced Zn$^{2+}$- and Mg$^{2+}$- ions. They are central symmetrical.

2. RESULTS AND DISCUSSION

The investigations of copper Jahn-Teller complexes in the single crystals of LiGa$_2$O$_4$, LiAl$_2$O$_4$ inversion and ZnAl$_2$O$_4$, MgAl$_2$O$_4$, ZnGa$_2$O$_4$, MgGa$_2$O$_4$ normal spinels at the 10 and 37 GHz and in the region of the temperatures T = 4-300K have been performed. The results of the investigation are given for the LiGa$_2$O$_4$. Because there are most full and allowed EPR spectra in this matrix. If we take not into account the inversion splitting, we shall observe the single line without the frequency and temperature dependence. If we do not take into account the inversion splitting, we shall observe a very complicated EPR spectrum. Such spectrum must have the characteristic frequency and temperature dependence. In the case S = 1/2 we shall have the three doublets and six levels in the magnetic field. We had to observe the five transitions in the low frequency region 1 [1]. There are three allowed transitions which correspond to the allowed $3^-\rightarrow 3^+$, $2^-\rightarrow 2^+$, $1^-\rightarrow 1^+$ and two forbidden $3^-\rightarrow 1^+$, $1^+\rightarrow 2^-$ transitions. This case corresponds to microwave frequency 10 GHz. Spectrum must contain one line for each from three potential minima corresponding to a distortion of the complex along one of the cubic axes. The intensity of these lines...
decreases with the increase of temperature. There appears an isotropic line. The investigations of the EPR spectra of the ions \( \text{Cu}^{2+} \) in LiGaO\(_2\) at frequency 37 GHz at T=4-300K have shown the presence of axial and isotropic spectrum which corresponds to intermediate region 2\(^1\). The axial spectrum is the static spectrum of the Jahn-Teller effect. We have found the following spin Hamiltonian parameters: \( g_{||}=2.386\pm0.002; \ A=111\pm2\ \text{Oe}; \ g_{\perp}=2.082\pm0.003; \ B=0 \). The spectrum is in the temperature region \( T=4-200\text{K} \). The hyperfine structure of the spectrum is at \( T=4-150\text{K} \). The isotropic spectrum is the dynamic spectrum of the Jahn-Teller effect. The temperature region of the existence of the spectrum is \( T=30-300\text{K} \), \( g=2.176\pm0.007 \). The maximum intensity of this isotropic spectrum is observed at \( T=110\text{K} \). The investigation of the EPR spectra of the ions \( \text{Cu}^{2+} \) in LiGaO\(_2\) at frequency 10 GHz allowed to observe the whole complex of lines which correspond to the transitions which are described in the inversion splitting theory by I.B.Bersuker. The three observed spectra (1, 2 and 3) correspond to above-mentioned allowed transitions. The two observed spectra 4 and 5 correspond to forbidden transitions. The two spectra 1 and 2 can be described by an axial spin Hamiltonian with \( S=1/2 \) and \( I=3/2 \). It has the following spin Hamiltonian parameters: \( g_{||}=2.379\pm0.002; \ A=90\pm2\ \text{Oe}; \ g_{\perp}=2.074\pm0.003; \ B=26\pm2\ \text{Oe} \). The parallel orientation of the spectra coincides with \( a<100> \) direction. The spectrum 1 at the \( T=8.5\text{K} \) is very good allowed in parallel (lines 1-4) and perpendicular (lines 5-8) orientations. The other lines at the \( T=8.5\text{K} \) are not observed. The spectrum 1 describes the an octahedron distorted along one of the three four-fold axes by the Jahn-Teller effect at low temperature. It characterizes the static Jahn-Teller effect. Therefore it is called the static (S) spectrum. Its intensity decreases when temperature increases. The spectrum 2 appears when the intensity of the spectrum 1 starts decreasing. The spectrum 2 correspond to \( 3^-3^+ \) transition of the excited intermediate doublet of the ground state ion \( \text{Cu}^{2+} \). The intensity of the spectrum 2, by comparison with the temperature of the spectrum 1, increases with the increase of temperature. Therefore it is called the dynamic (D1) spectrum. At \( T=18\text{K} \) the spectrum D1 is very good allowed in parallel (lines 9-12) and perpendicular (lines 13-16) orientations. It has the following spin Hamiltonian parameters: \( g_{||}=2.343\pm0.002; \ A=85\pm2\ \text{Oe}; \ g_{\perp}=2.018\pm0.002; \ B=55\pm2\ \text{Oe} \). The spectrum 3 appear at \( T=36\text{K} \). It is isotropic and correspond to \( 2^-2^+ \) transition of the upper doublet of the ground state ion \( \text{Cu}^{2+} \). The intensity of the spectrum D2, by comparison with the intensity of the spectrum 1, increases with the increase of the temperature. Therefore it is called the dynamic (D2) spectrum. The spin Hamiltonian parameters of the spectrum 3: \( g=2.138\pm0.003; \ A=55\pm2\ \text{Oe} \). The growth of relative intensities of the dynamic spectra D1 and D2 at the increase of temperature corresponds to the increase of Boltzman population of the excited intermediate and upper doublet states. The upper doublet is separated from the ground state by slot and has isotropic EPR spectrum. The forbidden spectra 4 and 5 (F) are observed in parallel orientation. In paper \[2\] it is reported about of possibility of the clear observation of such transitions with the magnetic field along \( a<111> \) direction. We observed such transitions. The intensity of the F-spectra, by comparison with the intensity of the ground spectra, increases with the increase of temperature.

### 3. CONCLUSIONS

We have succeeded in the observation of the whole complex of spectra which corresponds to the theory of the inversion splitting at the low frequency 10 GHz and at the high frequency 37 GHz. The role of the mechanism of dynamic narrowing of the resonance lines and of the mechanism connected with population of the excited states in the formation of the EPR spectrum and its temperature and frequency transformations is analysed.

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### 5. References
