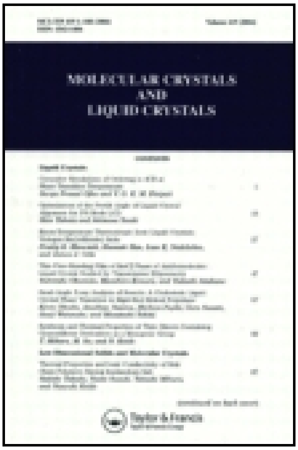

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Temperature Induced Change in Epr Spectrum of Fe 3+ Ion in the Complex of Iron with 2-Hydroxy-1-Nitrozonaphthalene

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TEMPERATURE INDUCED CHANGE IN EPR SPECTRUM OF Fe^{3+} ION IN THE COMPLEX OF IRON WITH 2-HYDROXY-1-NITROZONAPHTHALENE

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In temperature interval $T = 4.2 \div 290\,K$ in polycrystalline substance-2-hydroxy-1-nitrozonaphathalene $Na[Fe(C_{10}H_6ONO)_3]$, the EPR spectrum of Fe^{3+} has been investigated. The EPR spectrum is a superposition of two resonance lines and the non-resonance absorption. At the temperature change the redistribution of the absorption between the resonance lines takes place. The resonance line 1 with the effective g-factor $g_1 = 4.32 \pm 0.02$ has a maximal intensity at $T = 4.2\,K$. The resonance line 2 with the effective g-factor $g_2 = 2.00 \pm 0.01$ has the maximal intensity at $T = 290\,K$. With rising of temperature the integral intensity of the line 1 is decreasing, while intensity of the line 2 increasing. The second peculiarity of the temperature changes in the EPR spectrum of Fe^{3+} in the $Na[Fe(C_{10}H_6ONO)_3]$ is the exponential increasing of the linewidth for resonance line 2 when the temperature is lowered. The properties of EPR spectrum manifested in complex of iron with 2-hydroxy-1-nitrozonaphathalene are characteristics of the magnetic centers with multiple-minimum potential.

Keywords: EPR-spectrum; temperature change; organic complex of iron; magnetic centers; multiple-minimum potential

INTRODUCTION

In references [1–4], an unusual temperature dependence of the EPR spectrum of Fe^{3+} ion has been manifested in the organic substances (polyaniline and polyparaphenylene doped by Fe^{3+}, bromide cresol green, polycrystalline kaolinite). In these substances, the EPR spectrum is a superposition of two lines the behavior of which at temperature change is a contrast. When the temperature is lowered the intensity of first line is increasing, that of the second line – is decreasing in such a way that one of these has the maximum of intensity at low (helium) temperatures, the other – at room temperatures. The first line is the low-temperature (LT) EPR spectrum, second line – the high-temperature (HT) spectrum. A temperature change leads to a redistribution of the absorption intensities between the LT and HT spectra. This behavior of the EPR spectrum is an evidence of unusual dynamics of the molecules surrounding the Fe^{3+} ion. The presence of this dynamics may cause a substantial influence on various properties of the substance.

In addition, research of these dynamic transitions is of interest, since the magnetic centers exhibiting these properties are, as a rule, the systems with multiple-minimum potential. Among these systems the best studied is the Jahn-Teller system of a divalent copper ion in an octahedral environment [5].

The peculiarities of the magnetic centers with multiple-minimum potential develop in EPR spectra as a number of features: 1) the existence of a LT and HT spectra and 2) the redistribution of the intensity between LT and HT spectra at temperature change.

The summary orbital moment of the Fe^{3+} ground state is equal to zero. The electron-lattice interaction is absent. For this reason, the Jahn-Teller effect, in usual sense, should not be exhibited. In spite of this, the experimental results [1–4] confirm the development of the properties characterizing the magnetic centers with a multiple-minimum potential.

In present report, the EPR spectrum of the magnetic centers in $Na[Fe(C_{10}H_6ONO)_3]$ complex has been investigated.

EXPERIMENTAL RESULTS

Organo-metallic anionic complex of iron with 2-hydroxy-1-nitrozonaphathalene as sodium salt was synthesized and characterized in [6]. According to IR-, UV-spectroscopy, thermogravimetry and elemental analysis, the molecular formula of complex salt $Na[Fe(C_{10}H_6ONO)_3]$ has been confirmed. In this complex, the ferric ion is surrounded by three nitrozonaphthole ligands and connected with nitrogen and oxygen atoms of each ligand to form the pentagonal helate cycle [6], Figure 1.

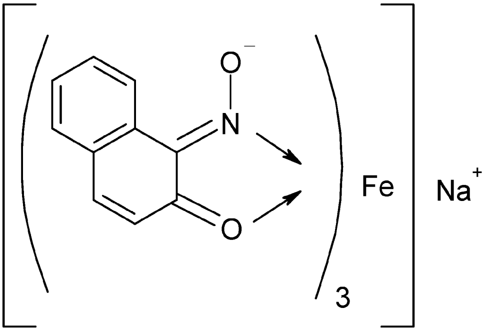

FIGURE 1 The molecular structure of 2-hydroxy-1-nitrozonaphathalene Na[Fe-($C_{10}H_6ONO)_3$].

According to data of X-ray powder diffraction [6], this complex salt has a low symmetry, its structure is monoclinic with lattice parameters: $a = 1.116$ nm; $b = 0.876$ nm; $c = 0.620$ nm; $\beta = 92.4°$.

The EPR spectrum was studied on an EPR spectrometer with a frequency of the microwave field $\nu = 9.246 \pm 0.001$ GHz in the temperature interval $T = 4.2 \div 290$ K.

In Figure 2 the lines of the EPR spectrum at temperatures of 4.2 and 290 K are shown. At $T = 4.2$ K a relatively narrow ($\Delta H_{pp} = 0.07$ kOe) line 1 is observed. The g-factor of line 1 is $g_1 = 4.32 \pm 0.02$. At $T = 290$ K a

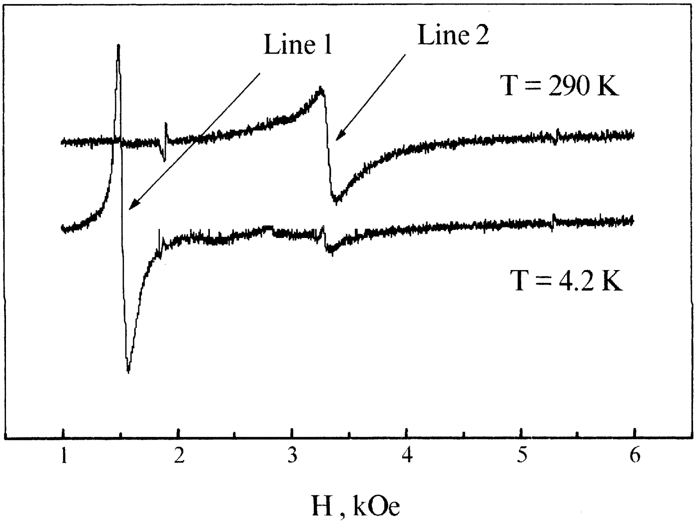

FIGURE 2 EPR spectrum of Fe^{3+} ion in Na[Fe($C_{10}H_6ONO)_3$].

broader ($\Delta H_{pp} = 0.16$ kOe) line 2 is observed. The *g*-factor of the line 2 is $g_2 = 2.00 \pm 0.01$. At intermediate temperatures the lines 1 and 2 are observed simultaneously. The increasing of temperature does not practically affect the width of the line 1. The width of line 2 is changed in unusual way. The width ΔH_{pp} for the line 2 is significantly increasing when the temperature is lower. In Figure 3 the shape of absorption lines of EPR spectrum for different temperatures are presented. The absorption lines are obtained by numerical integration of experimental lines, part of that are shown in Figure 2.

According to Figure 3 the temperature decrease leads to the redistribution of integral intensity of the lines so that at T = 290 K these remains only one resonance line 2. The *g*-factors of resonance lines 1 and 2 don't practically change with temperature. Analysis of the temperature

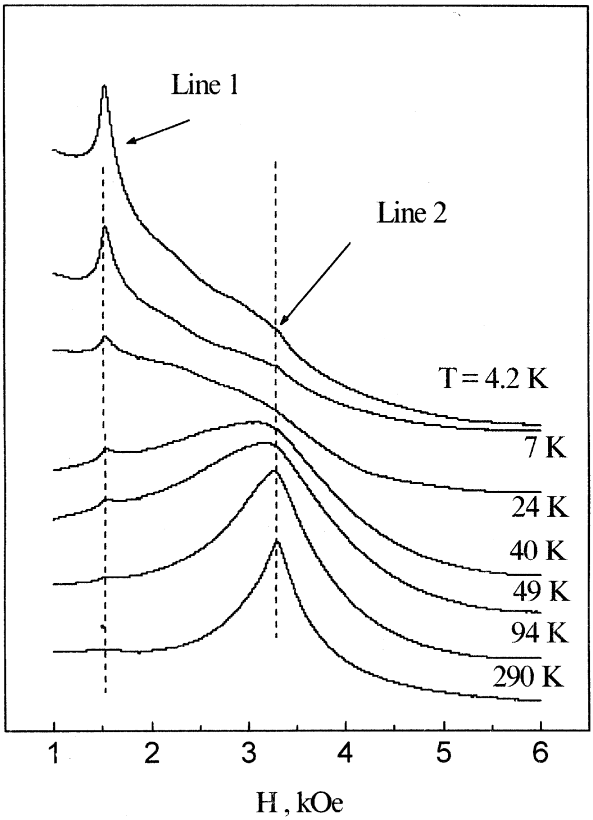

FIGURE 3 Absorption line shape for T = 4.2; 7; 24; 40; 49; 94 and 290 K.

dependence of the intensity of both lines reveals changes unusual for the spin-lattice relaxation mechanism. The conventional mechanism of line broadening caused by spin-lattice relaxation processes results in the increase of linewidth and the decrease of the peak intensity with temperature rise. At temperature increase, the intensity of the resonance line 1 of Figure 3 decreases till it completely disappears at $T = 290$ K. But at the same time the intensity of line 2 is, in contrast, increasing. The width of line 2 decreases, the width of line 1 does not change within the experimental error.

To quantitatively analyse the peculiarities of temperature-induced change in the spectrum a computer simulation of the absorption line has been carried out, and the decomposition of the observed line into components was done. The results of this decomposition for two extreme temperatures $T = 4.2$ K and $T = 290$ K are shown in Figure 4. From this figure one can see two resonance lines 1, 2 and non-resonance absorption. The intensity of the non-resonance absorption, the resonance lines 1, 2 and their shapes were calculated on condition of minimum deviation of the experimental absorption line from the simulated one obtained by theoretical calculation.

The temperature-induced change in EPR spectrum of Fe^{3+} may be described by two mechanisms. The first leads to usual decrease of the integral intensity of all contributions of the resulting absorption line at temperature increase. According to this mechanism, the temperature dependence of the integral intensity is described by equation $J(T) = J_0 * \tanh(h\nu/2kT)$, where ν is the frequency of radio-frequency field, k is the Boltzmann's constant. This mechanism is determined by temperature dependence of differences in occupation of resonance states. This mechanism is more strikingly demonstrated on the temperature dependence of line 1 shown in Figure 5. The second mechanism of temperature-induced change in the EPR spectrum defines the process of integral intensity redistribution between lines 1 and 2 (Fig. 3).

Apart from the peculiarities in the temperature-induced behavior of the intensity of resonance lines 1 and 2 in EPR spectrum of Fe^{3+} in $Na[Fe(C_{10}H_6ONO)_3]$, the unusual change of linewidth of line 2 is observed. This dependence is presented in Figure 6. On Figure 5 and Figure 6 the experimental points are obtained as a result of numerous resolutions of the resulting absorption line into components.

The unusual behavior of the intensity of the resonance line 1 and the width of resonance line 2 give reason to suppose that lines 1 and 2 are interconnected. At high temperatures only line 2 is observed. Therefore it may be called the "high-temperature" spectrum of Fe^{3+} magnetic centers in $Na[Fe(C_{10}H_6ONO)_3]$. The resonance line 1 appears at a lower temperature and achieves the maximum intensity at $T = 4.2$ K. Therefore it may be called the "low-temperature" EPR spectrum.

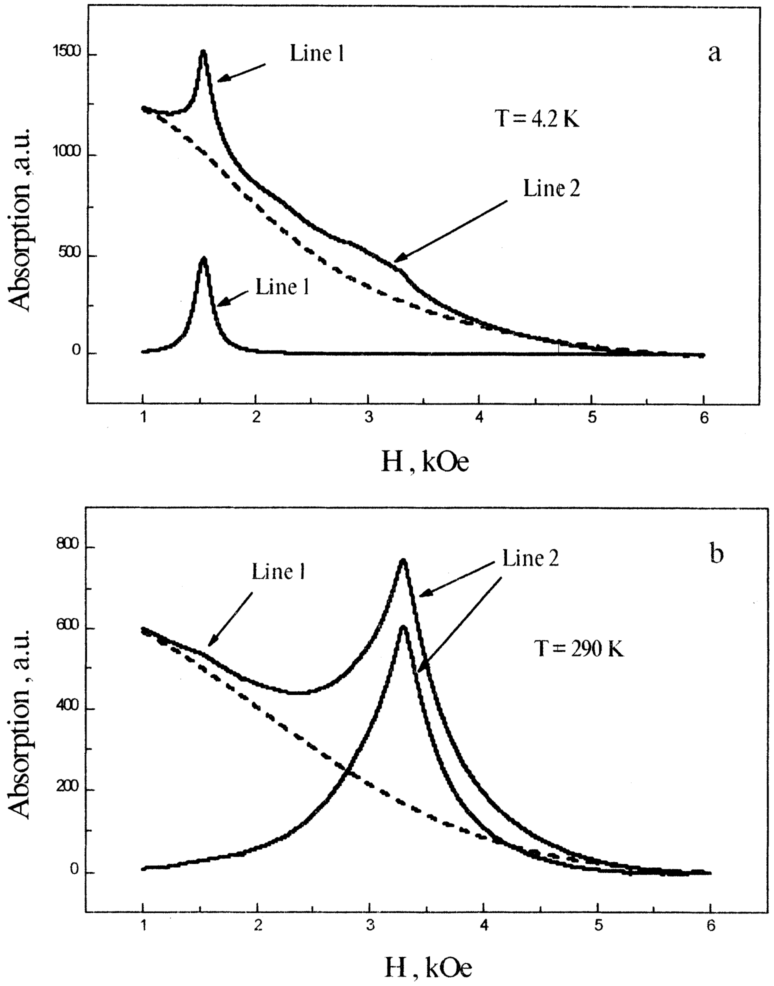

FIGURE 4 Decomposition of the resulting absorption line in Fe^{3+} EPR spectrum in $Na[Fe(C_{10}H_6ONO)_3]$ into component resonance lines 1, 2 and non-resonance absorption. The non-resonance absorption is shown by the dash line.

DISCUSSION OF THE RESULTS

The major fraction of iron ions in $Na[Fe(C_{10}H_6ONO)_3]$ are in the bivalent state. In substances containing bivalent iron there is, as a rule, always uncontrollable impurity of Fe^{3+} ions in small quantities. With the X-ray structure and electrochemical analysis of $Na[Fe(C_{10}H_6NO_2)_3]$ it has been

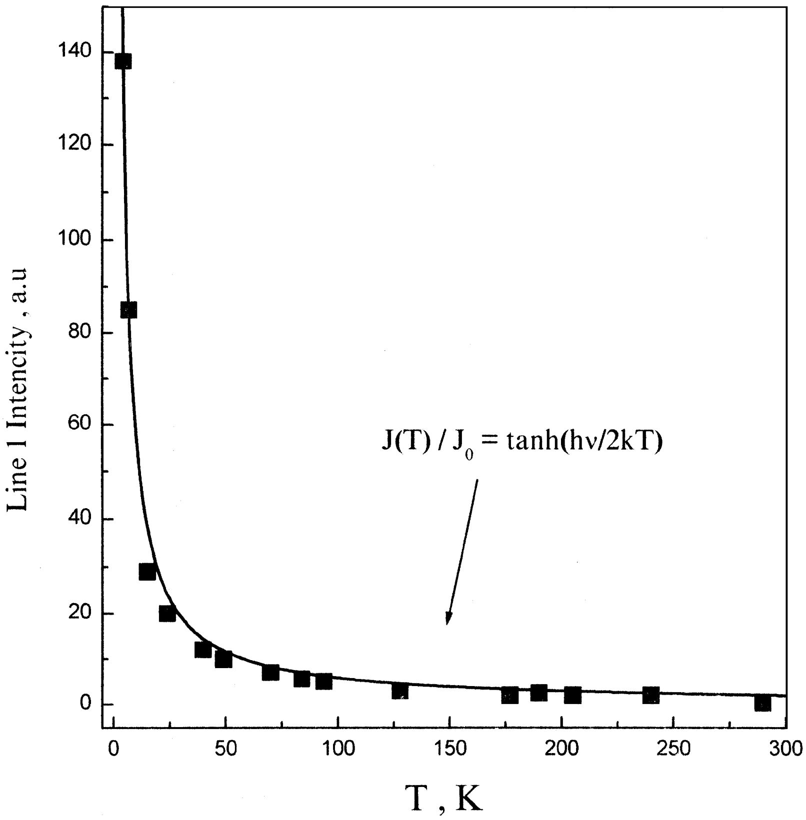

FIGURE 5 Temperature dependence of the integral intensity of line 1.

found that a part of Fe ions is in the trivalent state, which from the point of view of the energy is more stable than the bivalent one [6].

The Fe^{2+} ions more strongly interact with the crystalline environment as compared to the Fe^{3+} ions, therefore their relaxation properties differ essentially. The difference in relaxation properties results in different experimental conditions for the observation of their EPR spectra. For example, Fe^{2+} EPR spectrum is, as a rule, observed only at the liquid-helium temperature, whereas the Fe^{3+} EPR spectrum is observed in a wide temperature range from 4.2 to 300 K. Besides, in low-symmetry crystals, all the resonance lines of Fe^{2+} EPR spectrum highly depend on direction of external magnetic field. As a result, in polycrystalline sample, the orientational averaging of the anisotropic spectrum gives broader absorption lines in a wide range of magnetic fields. The described peculiarities result in

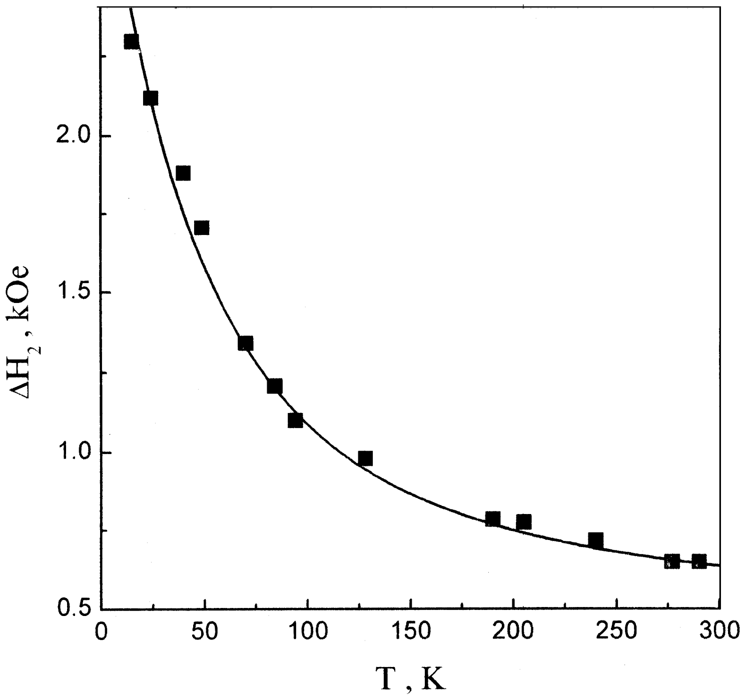

FIGURE 6 Temperature dependence of the width of line 2.

the fact that in polycrystalline sample the Fe^{2+} EPR spectrum is not observed experimentally.

EPR spectrum investigated in the present report consists of two resonance lines (Figs 2, 3). The first line with effective *g*-factor $g_1 \approx 4.3$, and the second line with $g_2 \approx 2.0$. The lines of EPR spectrum with such *g*-factors are characteristic of Fe^{3+} ions in the polycrystalline substances.

The resonance line with g-factor g_2 is characteristic of many magnetic centers, and Fe^{3+} ions too. Line 1 with g-factor g_1, in contrast to line 2, is the line characteristic only of ions with the spin $S = 5/2$. For example, the resonance line with $g = 4.3$ has been investigated in a number of studies [7–9] of the EPR spectrum of the iron ion in silicate glasses, which, like our complex, lack the long-range order. The similar analysis of the results of Fe^{3+} EPR spectra investigation in amorphous substances is given in [10]. In this paper it was shown that the spectrum which consists of two resonance lines with $g \approx 2$ and $g \approx 4.3$ belongs to Fe^{3+} ion. It was suggested [10] that resonance lines with such *g*-factors belong to different magnetic centers. The difference between centers is in the amount of low-symmetry component of the crystalline field acting on the magnetic ion. The line with $g \approx 2.0$ corresponds to center in which the low-symmetry component of the crystalline field is more less than the Zeeman energy. The line with $g \approx 4.3$ corresponds to center in which the low-symmetry component of "crystalline" field is more larger than the Zeeman energy.

The intensity of the EPR resonance line is proportional to the number of magnetic ions participating in given transition. The observed redistribution of the intensities of lines 1 and 2 (Fig. 3) attests to a change in the number of magnetic ions corresponding to these centers.

In [11] the analysis of possible mechanisms of the observed temperature dependence has been carried out. It was shown that a change in EPR spectrum can't be explained by temperature dependence of the zero-splitting parameters D and E. At strong temperature dependence of the parameters of spin Hamiltonian the EPR spectrum may consist of one resonance line, which at low temperatures is identical to line 1, and at high temperatures – to line 2. On the basis of computer simulation of the absorption line shape it was shown [11] that model of magnetic center with multiple-minimum potential gives a good agreement with experimental results.

The analysis of the temperature dependence of EPR spectrum, shown in Figure 3 and figures, presented in [11], allows one to conclude that the low-symmetry component of crystalline field acting on the Fe^{3+} ion in Na[Fe(C$_{10}$H$_6$ONO)$_3$] at low temperatures is more larger than the Zeeman energy, but at high temperatures it is more less. According to [11] the described temperature change in EPR spectrum may be explained not as transfer of Fe^{3+} ions from one non-equivalent position to another, but as transition of the magnetic center from one state to another.

Let us additionally mention a number of features observed for the studied magnetic centers: 1) the existence of a low-temperature, low-symmetry state and a high-temperature, high-symmetry state of the magnetic centers; 2) the presence of a temperature region in which the EPR spectra of both states are observed simultaneously; 3) a decrease of the intensity of the low-temperature spectrum and an increase of the intensity of the high-temperature spectrum as the temperature is raised.

The described character of the behavior of the magnetic centers is attributed to magnetic centers with multiple-minimum potential. For these systems the temperature-induced changes of intensity in EPR spectra corresponding to low-symmetry and high-symmetry states, are usually described by the model of "dynamic averaging" [12]. According to this model the spectrum and deformation are averaged as a result of fast "hops" of the system from one potential well to the other.

The coincidence of temperature-induced changes in EPR spectrum of Fe^{3+} ion in Na[Fe(C$_{10}$H$_6$ONO)$_3$] and well-studied systems with multiple-minimum potential allows one to suggest that molecules of Fe^{3+} ion surrounding have several energy-equivalent deformations, corresponding to low-symmetry of Fe^{3+} environment. In this case, the reason of unusual temperature change in the EPR spectrum is the peculiarity of the dynamics of the molecular environment of Fe^{3+} ion.

In the framework of the system with multiple-minimum potential we have been able to explain the unusual temperature dependence of resonance line 1 (Fig. 3) in EPR spectrum and unusual behavior of the linewidth of resonance line 2 (Fig. 6) and other features of the EPR spectrum.

At helium temperature the molecules of the environment are "frozen" at the bottom of potential wells in position corresponding to the largest value of low-symmetry component of the crystalline field. The anisotropy of the electric field is maximum, and therefore only resonance line 1 is observed. As the temperature is raised, some of the magnetic centers transit to excited vibronic states. The excited states of a system with multiple-minimum potential , as a rule, are less anisotropic than the ground state [5]. The overbarrier states (the states, whose energies are higher than the height of the barrier separating the potential wells [5]) are the least anisotropic. The occupation of the overbarrier states gives rise to an increase of contribution to resonance line 2 in the EPR spectrum (Fig. 3). Increasing the number of magnetic centers found in excited states will lead to a decrease in the number of magnetic centers in the ground states. This circumstance is the cause of the decrease of the intensity of resonance line 1 as the temperature is raised.

The unusual temperature dependence of the linewidth of resonance line 2 (Fig. 6) is connected to the distribution of magnetic centers by excited states. The higher the energy of excited states, the less the low-symmetry electric field of the magnetic ion. If the energy of excited state is higher than the barrier height between the potential wells (overbarrier states), the effect of this component becomes minimal or equal to zero.

At high temperatures many magnetic centers are found in overbarrier states. The EPR spectrum of these centers is determined by the g-factor of the transition $+1/2 \leftrightarrow -1/2$. The g-value of resonance line corresponding to this transition is near $g = 2.0$.

At low temperatures an appreciable fraction of the magnetic centers will be found in underbarrier excited states. The lower the excitation energy, the higher the low-symmetry component of the electric field, and the farther the resonance line of transitions $\pm 5/2 \leftrightarrow \pm 3/2$ from the line of the transition $+1/2 \leftrightarrow -1/2$. As a result of the orientation averaging over the directions of the symmetry axes, the contribution of the transitions $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$ at low temperature will lead to the broadening of resonance line 2. The lower the temperature, the larger the contribution to line 2 of the underbarrier excited states in comparison to overbarrier states. This is the reason for the broadening of resonance line 2 at temperature decrease.

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