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Abstract
The EPR (electron paramagnetic resonance) spectra of non-Jahn–Teller (JT) Mn^{2+} and JT Cu^{2+} ions have been studied for α- or β-LAS structure modification in the temperature range of 4.2–480 K. The experimental evidence for JT glass with frozen-in random strain fields due to the presence of the JT Cu^{2+} ions is presented.

1. Introduction

It has been predicted by Mehran *et al* [1] that: 'Jahn–Teller (JT) ions in crystals exert forces on their neighbours and are, thereby, indirectly coupled by Ising-type interactions' giving a condition for glass formation at low enough temperature. In 1988 Kumari *et al* [2] claimed tentatively the possibility of such JT phases in LiKSO$_4$, LiNaSO$_4$ and LiNH$_4$SO$_4$ crystals doped with Cu^{2+} ions.

In view of the present interest in spin and other glasses, the question arises as to whether a diluted system will show a JT glass phase. We restricted our investigation to lithium ammonium sulfate (LAS; LiNH$_4$SO$_4$) monocrystals doped with Mn^{2+} or Cu^{2+} ions.

The LAS crystal has been known of since 1868 [3] and its literature extends to over 200 papers. Nevertheless, it is sometime missed [2, 4] that LAS exists in two different polymorphic modifications, α and β [5, 6]. The α-form crystallizes at a temperature lower than 293 K [7] whereas the β-form of LAS grows above this temperature. X-ray and DTA investigations performed by Sosnowska *et al* [6] show that single crystals of the α-modification exhibit a phase transition at 255 K and that a transition from the α- to the β-modification of LAS takes place at about 350 K. This transition is found to be irreversible and characterized by slow kinetics.

The aim of our work is to provide a careful study of non-JT Mn^{2+} and JT Cu^{2+} ions in α- and β-LAS modifications.

The paper is organized as follows:

- Section 2 contains a short description of the α- and β-structures.

- Section 3 describes the sample preparation and experimental conditions.
- Section 4 describes Mn^{2+} electron paramagnetic resonance (EPR) spectra for α- and β-phases.
- Sections 5 and 6 describe Cu^{2+} EPR spectra for α- and β-phases.
- Sections 7 and 8 present the results, a discussion and conclusions.

2. α- and β-LAS crystal structures

The crystal structure of α-LAS is orthorhombic [8] with space group $Pca2_1$ and lattice parameters $a = 10.196$ Å, $b = 4.991$ Å and $c = 17.010$ Å. The structure is built of layers of LiO_4 and SO_4 tetrahedra connected by edges and corners placed perpendicularly to the [001] direction.

The β-LAS structure has a three-dimensional framework of LiO_4 and SO_4 tetrahedra. Thus the $\alpha \rightarrow \beta$ transformation requires the SO_4 tetrahedra to reorientate and a shift of the Li ions [9]. The NH_4 cations are located in the cavities of this framework. The β-LAS undergoes successive phase transitions at $T_1 = 462$ K from the paraelectric ($Pmcn$, $Z = 4$) to the ferroelectric phase ($Pc2_1n$, $Z = 4$), at $T_2 = 283$ K from the ferroelectric to the ferroelastic ($P2_1/c$, $Z = 8$) phase and at $T_3 = 28$ K to another ferroelastic phase (Cc) [6].

3. Sample preparation and experimental conditions

Single crystals of LAS doped with Cu^{2+} or Mn^{2+} ions were grown at 290 K by slow evaporation of an aqueous solution containing equimolar amounts of $(NH_4)_2SO_4$ and $Li_2SO_4 \cdot H_2O$ to which of 1 mol% of $MnSO_4 \cdot H_2O$ or $CuSO_4 \cdot H_2O$ was added. The crystals obtained were transparent and had a cleavage plane perpendicular to the a-axis.

The EPR measurements were performed with a CW X-band spectrometer (9.2 GHz) in the temperature range of 4.2–480 K. The orthogonal XYZ laboratory framework for the EPR line anisotropy pattern was chosen as follows: $X \parallel a$, $Y \parallel b$, $Z \parallel c$, where a, b, c are crystallographic axes. Both LAS:Mn^{2+} and LAS:Cu^{2+} are grown in the α-modification. After making measurements of spin-Hamiltonian parameters at room temperature (RT), the samples were cooled down to liquid helium (LH) temperature and EPR spectra were recorded.

4. The temperature dependence of $Mn^{2+}(^6S, d^5)$ EPR spectra

The Mn^{2+} spectrum (figure 1) is isotropic, with well-resolved hyperfine structure as for ions in the cubic crystal field symmetry, which is in agreement with the Reddy *et al* [10] optical data. The spectrum is described with a simple spin-Hamiltonian:

$$\hat{H} = \mathbf{g}\beta\mathbf{B}\hat{S} + \mathbf{A}\hat{I} \cdot \hat{S}, \tag{1}$$

where $\mathbf{g}$, $\mathbf{A}$ are the spectroscopic and hyperfine tensors, respectively, $\hat{I}$, $\hat{S}$ are the nuclear and electron spin operators, with isotropic $g = 2.001$ and $A = 98$ G.

Below RT down to LH temperature, the hyperfine structure of Mn^{2+} is smoothly washed out due to linewidth growth of individual hyperfine components. Figure 2 shows the temperature evolution of the Mn^{2+} EPR spectrum for the temperature run RT $\rightarrow$ 480 K $\rightarrow$ 116 K. At about 410 K at the central part of the spectrum a new line with $\Delta H_{pp} \cong 110$ G appeared. This line is caused by the Mn^{2+}–Mn^{2+} exchange interaction J which is of the order of $2A \cong 0.020$ cm^{-1}. We will show a possible exchange path in section 7.
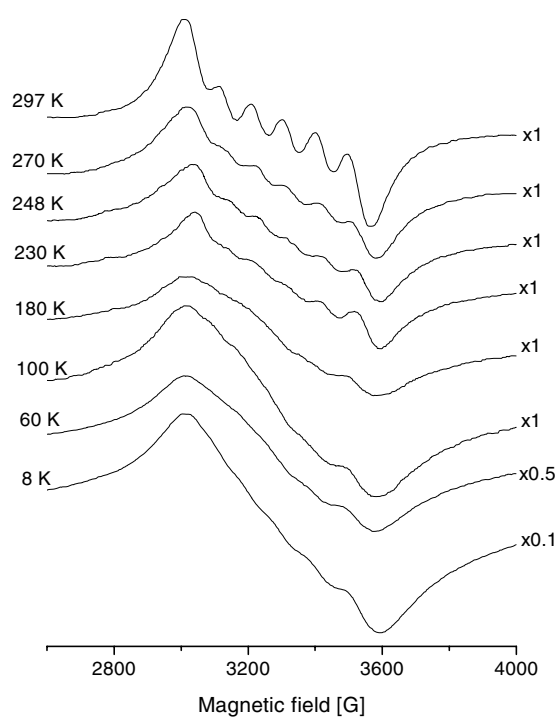
Figure 1. EPR spectra of Mn^{2+} in α-LAS recorded in the temperature range of 297–8 K.

5. EPR spectra of α-LAS:Cu^{2+} at RT

The EPR spectra of $Cu^{2+}(^2D, d^9)$ ions consist of three broad, slightly anisotropic lines. At RT, three curves are converted to two broad ones with ΔH_{pp} of the order of 100 G (see figure 3(a)).

The g-value parameters at RT evaluated from the spin-Hamiltonian (1) are $g_z = 2.33(1)$, $g_y = 2.21(3)$ and $g_x = 2.17(3)$.

Computer structure generation for LAS, together with the EPR data, allows us to determine the position of the Cu^{2+} ion as the interstitial position between two NH_4 vacancies. This is the same position as for the Mn^{2+} ion. The Cu^{2+} ion is a typical JT ion and the symmetry of its crystal field is a result of JT static deformation.

6. The temperature dependence of Cu^{2+} spectra

The EPR spectra recorded versus temperature for α-LAS:Cu^{2+} oriented along the Y-axis in response to an external magnetic field are shown in figure 3. The first temperature run, $290 \rightarrow 100 \rightarrow 290$ K (figure 3(a)), gives fully reproducible spectra. But this is not the case for the second temperature run (figure 3(b)), $290 \rightarrow 400 \rightarrow 290$ K. At about 350 K, where the $\alpha \rightarrow \beta$ transformation is expected, the EPR line is broadened and then, at about 380 K, the spectrum is transformed to a 'powder-like' one, with $g_\parallel = 2.40$ and $g_\perp = 2.09$. This spectrum persists down to LH temperature. If the sample, after the RT $\rightarrow$ 400 $\rightarrow$ RT temperature run, is stored at RT for about 150 h, its 'powder-like' spectrum is transformed to a 'crystal-like' slightly anisotropic one (figure 3(d)). Next, the sample was heated to 470 K (figure 3(c)) and
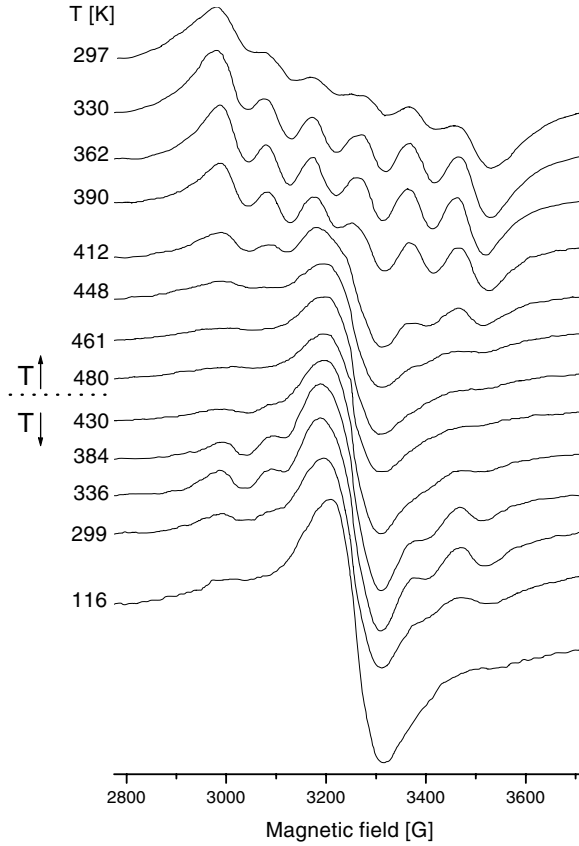
Figure 2. Mn^{2+} EPR spectra for LAS recorded after two temperature cycles: 290–480 and 480–116 K.

cooled down to 290 K and, after 10 min, again a 'powder-like' spectrum was recorded as shown in figure 3(e). Optical inspection of all samples used did not reveal any cracking or inclusions.

This anomalous—and to our knowledge, seldom observed in crystals [11]—Cu^{2+}-ion behaviour is in our case caused by the Cu^{2+} JT interaction with the β-LAS lattice. Because the Cu^{2+} and Mn^{2+} ions replace two NH_4 vacancies in the LAS structure, they should be in crystal fields of cubic symmetry. Three lines of Cu^{2+} at low temperature appear as the result of the static JT effect. The g-value temperature evolution is shown in figure 4 for three JT centres.

At about 350 K, three lines collapse to an isotropic one with average $\langle g \rangle = 2.237$. At low temperature, three relatively perpendicular octahedra deformations are described by the following g-factors [12]:

$$g_1 = 2 - \frac{2\lambda}{\Delta}\left(\cos\frac{\phi}{2} - \sqrt{3}\sin\frac{\phi}{2}\right)^2,$$
$$g_2 = 2 - \frac{2\lambda}{\Delta}\left(\cos\frac{\phi}{2} + \sqrt{3}\sin\frac{\phi}{2}\right)^2, \tag{2}$$
$$g_3 = 2 - \frac{8\lambda}{\Delta}\cos^2\frac{\phi}{2},$$

where λ is the spin–orbit coupling constant, Δ is the first excited orbital level, ϕ is the azimuthal angle of the normal coordinate for the Q_1- and Q_2-octahedra.
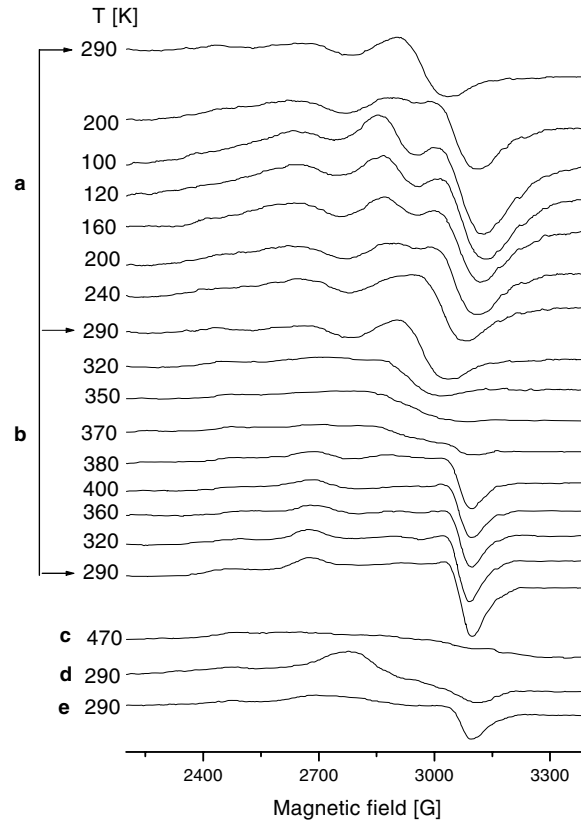
Figure 3. EPR spectra of Cu^{2+} in LAS. (a) α-LAS: temperature run 290–100–290 K; (b) $\alpha \rightarrow \beta$-LAS: 290–400–290 K; (c) at 470 K; (d) after 150 h storage at RT; (e) after 10 min heating at 470 K.

At high temperature, where the frequency of vibration $\nu > \nu_{EPR}$, the following conditions are valid in equation (2):

$$\left\langle \cos^2 \frac{\phi}{2} \right\rangle = \left\langle \sin^2 \frac{\phi}{2} \right\rangle = \frac{1}{2},$$
$$\left\langle \cos \frac{\phi}{2} \sin \frac{\phi}{2} \right\rangle = 0,$$
(3)

and as a result the average g-value is equal $\langle g \rangle = (1/3)(g_z + g_y + g_x) \cong 2.237$ as shown in figure 4.

7. Results and discussion

The essential difference between the α- and β-LAS modifications is that at about 350 K, the β-phase crystal lattice dimensionality changes from two to three dimensional due to SO_4 and LiO_4 tetrahedra rotation and shift of the Li ions.

Figure 5 presents our computer generation of the β-LAS crystal structure in accord with the Itoh *et al* [13] x-ray data.
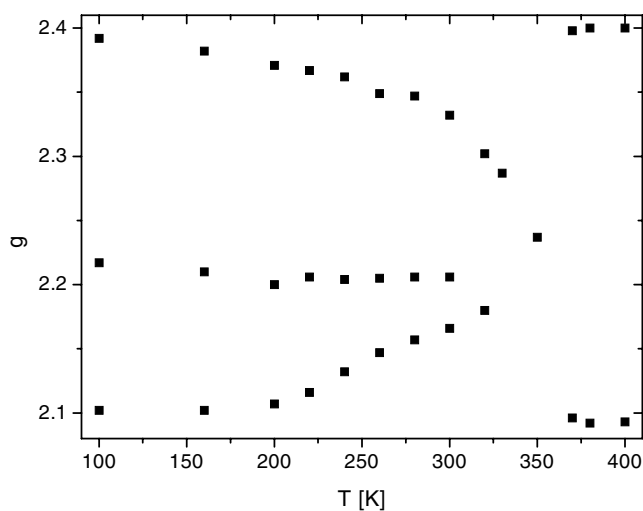
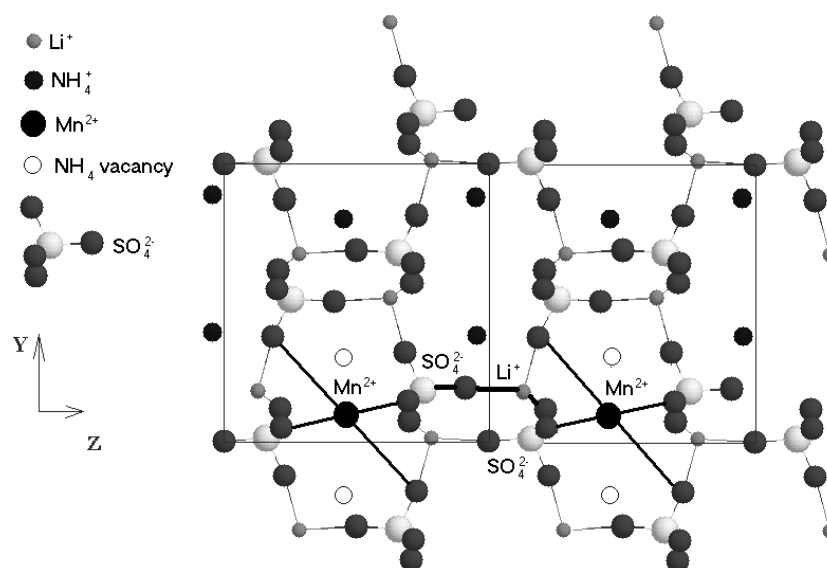**Figure 4.** The temperature dependence of the g-value for Cu^{2+} EPR spectra (as shown in figure 3).

Figure 5. A fragment of the β-LAS structure with the path of Mn^{2+}–SO_4–Li–SO_4–Mn^{2+} exchange marked.

The EPR spectra of Mn^{2+} ions in the β-phase show Mn^{2+}–Mn^{2+} pair exchange, caused most probably by the weak interaction across the Mn^{2+}–SO_4–Li–SO_4–Mn^{2+} path (figure 5).

In the case of β-LAS:Cu^{2+} we deal with randomly quenched JT centres where only 'short-range order' is formed. This real situation reminds us of the results obtained by Klenin [14] in computer experiments, showing that intermolecular quadrupole interaction on the same lattices can lead to a short-range rotational 'freezing' similar to spin-glass ordering. A similar effect was predicted for strain defects in alkali halides [15]. On the other hand, Mehran *et al* [1] posed the question of whether a diluted JT system will show a JT glass phase. Murthy *et al* [2]

claimed that their data for Cu^{2+} ions in $LiKSO_4$, $LiNaSO_4$ and $LiNH_4SO_4$, with 'powder-like' spectra of the low-temperature phase, i.e. below 247 K, indicate such a JT glass for diluted JT systems with randomly frozen-in strain fields. The authors [2] did not state which type of LAS (α or β) was investigated. It is also unclear why their EPR spectra are isotropic at RT in contrast to ours.

Our experiments on LAS:Cu^{2+}, repeated several times, show unambiguously that only β-LAS with Cu^{2+} reveals such JT short-range-ordered glassy behaviour in the temperature range which includes the phase transition temperature for pure β-LAS.

Most probably, the molecular mechanism leading to such random freezing of JT Cu^{2+}-ion deformation is connected with electrical conductivity. The dc electrical conductivities of pure and Cu^{2+}-doped, quenched samples of β-LAS were measured by Syamaprasad and Vallabhan [16] between 77 and 563 K; Λ-type conductivity anomalies were recorded at 286 and 455 K. The comparison of the conductivities for pure and doped LAS prompts the suggestion that migrating interstitial Li^+ ions dominate the mechanism of electrical transport. In β-LAS, random breaking of Li–O bonds causes short-range ordering of Cu^{2+} clusters—recorded as a 'powder-like' spectrum. The argument for such a mechanism is that a brief (10 min) heating of crystal at 470 K transforms 'powder-like' spectra to 'crystal-like' ones, because raising the temperature increases the Li^+-ion mobility and destroys 'quenched' Li–Cu clusters (random freezing of the JT strains).

8. Conclusions

Our comparative EPR studies of LAS crystals doped with non-JT Mn^{2+} and JT Cu^{2+} ions reveals that:

 (i) Both ions occupy interstitial positions in LAS with cubic symmetry of the crystal field.
 (ii) The crystal field deformation of the Cu^{2+} ion is caused from RT down to LH by static JT deformation.
(iii) At about 350 K, where an irreversible $\alpha \rightarrow \beta$ crystal transformation appears, the crystal lattice transforms from two to three dimensionality. The Mn^{2+} EPR spectra reflect the weak coupling of the Mn^{2+}–Mn^{2+} pairs.
(iv) The Cu^{2+} spectrum above 350 K is a dynamically averaged JT spectrum.
 (v) At about 370 K, the Cu^{2+} 'powder-like' spectrum reflects the short-range order of the JT glass.
(vi) The molecular reason for that is a local strain freezing due to Li^+-ion mobility.

According to Mehran *et al* [1], the essential requirement for a glass is that the effective Ising exchange interaction in the Hamiltonian of the JT cooperative effect should appear with both positive and negative signs. Such deformations with equal strengths and opposite signs may be ensured by b_{1u} and b_{2g} deformation modes [17].

At the very least, we have found analogies of the Ising spin-glass caused by JT ions in the frozen-in random strains in ferroelastic β-LAS.

Acknowledgment

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