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On a correlation between EPR data for SASeD doped with Cr^{3+} and soft modes

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EPR experimental results obtained for SASeD doped with Cr^{3+} are reported with special emphasis on those observations which reveal the effect of soft modes i.e. the temperature dependence of the D_{ZZ} spin-Hamiltonian parameter and the temperature dependence of the EPR linewidth. An extension of the two-sublattice model, previously developed and tested for SASD, to include lattice vibrations is presented. The obtained spectrum of bound excitations for the system investigated supports the idea that soft modes contribute to the phase transition at $T_{\mathrm{C}} = 175$ K. The anomaly detected at $T_1 = 150$ K has only a quasisoft mode character and the anomaly detected at $T_2 = 280$ K cannot be related to the effect of soft modes.

Key words: *sodium ammonium selenate dihydrate, EPR, soft modes, phase transitions*

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1. Introduction

Sodium ammonium selenate dihydrate (SASeD) crystals have been investigated for many years. Perhaps the most complete account of the properties of SASeD is given in the paper by Aleksandrov et al. [1]. Below, we quote only a part of the information given in [1] needed for the purpose of this paper. Below $\mathrm{T_c} = 175$ K the crystal becomes ferroelectric. The transition from paraelectric phase (with a space group $P2_12_12_1$) to ferroelectric phase (with a space group $P2_1$) is of the first order. It was also recognized that molecular rotations of two inequivalent groups ($\mathrm{SeO_4}$ (I)) and ($\mathrm{SeO_4}$ (II)) to a great extent contribute to the appearance of spontaneous polarization P_{S} [2,3]. However the effect of soft modes in the phase transition of SASeD has not been described so far. It is the aim of this paper to report how the effect of soft modes reflects in the temperature dependence of the EPR spectrum of SASeD doped with Cr^{3+} and how the theory developed by us and described in [4] can be extended to include dipole interactions with the crystal lattice.

2. Experimental

Large and good quality single crystals of SASeD doped with Cr^{3+} were grown using the method of evaporation of equimolar solution of $\mathrm{NaNH_4}SeO_4$ and $\mathrm{Cr}(SO_4)\cdot 18\mathrm{H_2O}$. The growth procedure was kindly carried out by Prof. Czapla from Wroclaw University.

EPR spectra of the grown material were recorded using a standard EPR X-band spectrometer with 100 kHz modulation of the steady magnetic field. The measurements were carried out in the temperature range from 300 K down to 120 K using a liquid nitrogen cryostat.

3. Experimental results

The EPR spectrum of SASeD doped with Cr^{3+} is shown in figure 1. It could be parameterized using a standard spin-Hamiltonian:

$$\hat{H} = \mu_{\mathrm{B}} \vec{S}\, \vec{g}\, \vec{H} \;+\; \hat{S}\, \overleftrightarrow{D}\, \vec{S} \tag{1}$$

with $S = 3/2$.

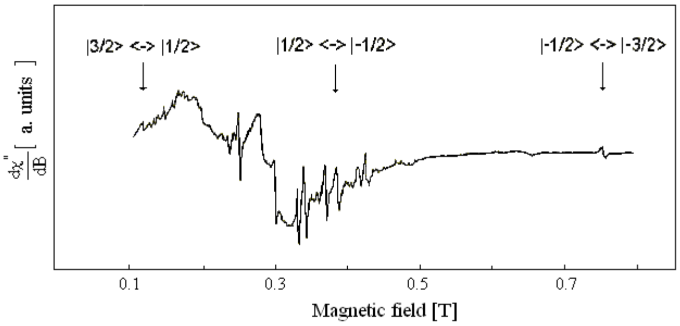

Figure 1. The EPR spectrum of SASeD:Cr^{3+} recorded at room temperature for $\vec{B}|$z. The allowed electronic transitions are indicated by arrows.

Temperature dependence of D_{ZZ} parameter is shown in figure 2. Three temperature points at which the $D_{ZZ}(T)$ function behaves specifically can be distinguished: one about 150 K, the other at about 175 K, and the last one at about 280 K. Obviously, the anomaly observed at 175 K corresponds to the transition point T_{C}. This temperature is about 5 K lower than T_{C} determined from dielectric measurements. The reasons for the existence of the other two anomalies can be explained in the way it was done for sodium ammonium sulphate dehydrate (SASD) in [3].

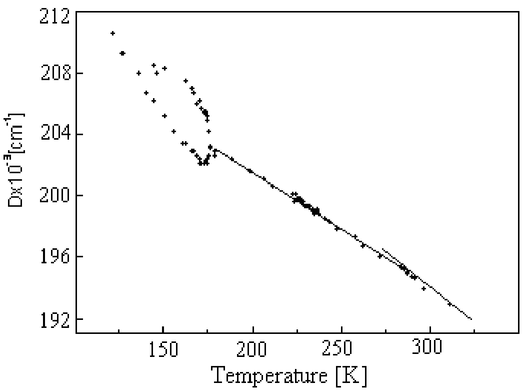

Figure 2. Temperature dependence of the D_{ZZ} spin-Hamiltonian parameter.

The role of soft modes reflects in the temperature behaviour of D_{ZZ} below 175 K. According to Owens [5], the softening of the phonon mode for the systems exhibiting the first order phase transition and lacking a centre of inversion should lead to the following temperature dependence of D_{ZZ}:

$$D_{ZZ} = aT \pm b\sqrt{T_{\mathrm{C}} - T}\,. \tag{2}$$

This type of functional dependence is seen in figure 2 in close vicinity of $T_{\mathrm{C}} = 175$ K.

Figure 3 shows the temperature dependence of the EPR linewidth for $T > T_{\mathrm{C}}$. The measurements were carried out for the line corresponding to the $-3/2 \leftrightarrow -1/2$ electronic transition. As

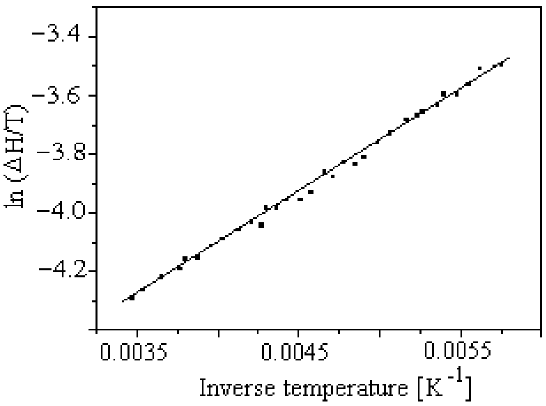

Figure 3. Temperature dependence of the EPR line for $T > T_{\mathrm{C}}$ and the best fit to equation (3).

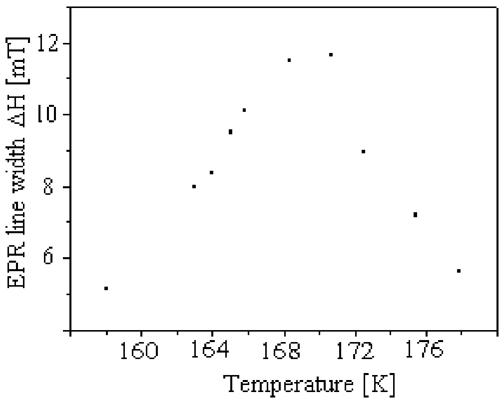

Figure 4. Temperature dependence of the EPR line width in close vicinity of T_{C}.

seen in figure 1, this line is distinctly separated from the rest of the spectrum and therefore it almost perfectly suits such studies.

Figure 3 clearly shows that the linewidth broadens with the temperature decrease contrary to the case expected for isolated Cr^{3+} ions in a diamagnetic host lattice. Following Owens [6] we assumed that this phenomenon can be explained in terms of zero-field fluctuations caused by molecular movements of polar groups. In this case, the EPR linewidth is functionally described by:

$$\Delta H = T\,\chi(0)\,\tau_{\mathrm{C}}\exp\left(-\frac{E}{kT}\right), \tag{3}$$

where $\chi(0)$ is a low frequency limit of magnetic susceptibility, τ_{C} is correlation time. The best fit of experimental data to the above relation enabled us to define the activation energy $E = 0.0301$ eV.

For $T < T_{\mathrm{C}}$ the EPR linewidth should be proportional to $(T_{\mathrm{C}} - T)^{-1/2}$. The temperature dependence of the EPR linewidth in the temperature range close to T_{C} is shown in figure 4. It can be seen that, at least qualitatively, the experimental results support the idea of substantial contribution of soft modes to the nature of phase transition for SASeD.

4. Theoretical considerations

In our previous paper [7] we studied in detail the contribution of two active groups $SO_4\,(I)$ and $SO_4\,(II)$ to both the phase transition and to two experimentally observed anomalies for SASD.

The same Hamiltonian can be used to investigate the similar behaviour of SASeD:

$$\tilde{H} = H_0 + H_1\,, \tag{4}$$

where

$$H_0 = -\sum_{i=1}^{N}\left\{\sum_{f=1}^{2}\left[\Gamma_f S_{fi}^x + (\Delta_f + p_0 E)\,S_{fi}^z\right] + K S_{1i}^z S_{2i}^z\right\}, \tag{5}$$

$$H_1 = -\frac{1}{2}\sum_{ij=1}^{N}\left\{J_{ij}\left(S_{1i}^z S_{1j}^z + S_{2i}^z S_{2j}^z\right) + K_{ij}\left(S_{1i}^z S_{2j}^z + S_{2i}^z S_{1j}^z\right)\right\}. \tag{6}$$

Here H_0 describes one-particle energy and H_1 describes the interaction between different particles. However, in order to include a correlation between lattice vibrations and the process of ordering occurring in the crystal under discussion one should add to (4) yet another two terms:

$$H_\mathrm{l} = \sum_{k,a} \hbar\omega_a(\vec{k})\beta^+_{ka}\beta_{ka}, \tag{7}$$

$$H_\mathrm{int} = \sum_{i,f,k,a} \tau_{af}\mathrm{e}^{\mathrm{i}\vec{k}\vec{R}_i} S^z_{fi}\left(\beta_{ka}+\beta^+_{-ka}\right). \tag{8}$$

H_l corresponds to free phonon energy of the crystal lattice and H_int corresponds to pseudospin-lattice interaction. The following designations were used in (5)–(8): i is the lattice cell number; f is the number of sublattice (in every cell); a is the number of the branch of lattice vibration; Γ is the tunnelling constant for motion of SeO_4 group through a potential barrier; Δ_f is the height of this barrier; p_0 is the dipole momentum of the active groups; E is the external electric field; J_{ij}, K_{ij} are constants of interaction for particles from the same sublattice (J_{ij}) and from different sublattices (K_{ij}), $K = K_{11} = K_{22}$, $\omega_a(\vec{k})$ is the cyclic frequency of a-branch of lattice vibration with a fixed wave vector $\vec{k}$; S^x_{fi}, S^z_{fi} are spin operators, β_{ka}, β^+_{ka} are phonon operators.

The potential barrier Δ_f for the crystal structure of SASeD can be taken in the form (see [3,7]):

$$\Delta_1 = \Delta + \delta P, \qquad \Delta_2 = -\Delta + \delta P, \tag{9}$$

where δ is an asymmetric constant and P is a polarization of the crystal.

In the selfconsistent field approximation $H_0 + H_1$ reduces to the following representation:

$$H_0 + H_1 = \begin{pmatrix} A_1 & \Gamma & \Gamma & 0 \\ \Gamma & A_2 & 0 & \Gamma \\ \Gamma & 0 & A_3 & \Gamma \\ 0 & \Gamma & \Gamma & A_4 \end{pmatrix}. \tag{10}$$

Here:

$$\begin{aligned}
A_1 &= -K - 2(\delta + J_1)P - 2p_0E, \\
A_2 &= K - 2\Delta - 2J_2\xi, \\
A_3 &= K + 2\Delta + 2J_2\xi, \\
A_4 &= -K + 2(\delta + J_1)P + 2p_0E, \\
J_1 &= \sum_j (J_{ij} + K_{ij}), \qquad\qquad P = \frac{1}{2}\langle S^z_{1i} + S^z_{2i}\rangle, \\
J_2 &= \sum_j (J_{ij} - K_{ij}); \qquad\qquad \xi = \frac{1}{2}\langle S^z_{1i} - S^z_{2i}\rangle; \\
\langle\ldots\rangle &= \frac{\mathrm{Tr}\left[\cdots \mathrm{e}^{-\beta(H_0+H_1)}\right]}{\mathrm{Tr}\left[\mathrm{e}^{-\beta(H_0+H_1)}\right]}, \qquad \Gamma = \Gamma_1 = \Gamma_2.
\end{aligned} \tag{11}$$

Diagonalization of (4) may be obtained using a unitary transformation:

$$W^{-1}(H_0 + H_1)W = H_\mathrm{diag}, \tag{12}$$

The matrix elements of W were calculated and we obtained the following pseudospin-lattice Hamiltonian convenient for further calculations:

$$H = \sum_{i,n}\Lambda_n X^{nn}_i + \sum_{k,a}\hbar\omega_a(\vec{k})\beta^+_{ka}\beta_{ka} + \sum_{i,f,k,a}\sum_{m,n}\alpha^{(f)}_{mn}X^{mn}_i\tau_{af}\mathrm{e}^{\mathrm{i}\vec{k}\vec{R}_i}\left(\beta_{ka}+\beta^+_{-ka}\right). \tag{13}$$

In the above expression Λ_n are the eigenvalues of (4), X^{mn}_i are the Hubbard operators and $\alpha^{(1)}_{mn}$, $\alpha^{(2)}_{mn}$ are the matrix elements of a transformed $\tilde{\sigma}^z_f$ spin-like operators:

$$\begin{aligned}
\tilde{\sigma}^z_1 &= W^{-1}(S^z \otimes I)W, \qquad \tilde{\sigma}^z_2 = W^{-1}(I \otimes S^z)W; \\
S^z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},
\end{aligned} \tag{14}$$

$\otimes$ is the symbol of a direct product.

In order to study the dynamics of a bound pseudospin-lattice system the method of double-time Green functions [8] was used.

As a result we obtained the following relation describing the functional dependence of the bound phonon-dipole excitations upon the temperature:

$$\begin{aligned}\left(E^2-\hbar^2\omega_1^2\right)\,(E-\Lambda_{mn}) \;&=\; 128\,\hbar\,\omega_1\,\tau_{11}^2\,\frac{(\Delta+J_2\xi)^2\,(\Lambda_m+\Lambda_n)^2}{\eta_m^2\,\eta_n^2}\left[\Lambda_m^2\Lambda_n^2-4\left((\delta+J_1)\,P+p_0E\;\right)^2\right.\\&\quad\left.\times\left(\Lambda_m^2+\Lambda_n^2\right)+16\left((\delta+J_1)\,P+p_0E\right)^4\right]^2\langle X^{mm}-X^{nn}\rangle\,. \qquad (15)\end{aligned}$$

In the above expression

$$\begin{aligned}\eta_n \;&=\; 2^{1/2}\left\{\left[\Lambda_n^2-4\left((\delta+J_1)\,P+p_0E\right)^2\right]^2\left[\Lambda_n^2+4\,(\Delta+J_2\xi)^2\right]\right.\\&\quad\left.+\,4\,\Gamma^2\Lambda_n^2\left[\Lambda_n^2+4\,\left[(\delta+J_1)\,P+p_0E\right]^2\right]\right\}^{1/2}. \qquad (16)\end{aligned}$$

As seen in figure 5, at $T_{\mathrm{C}}=175$ K the excitation energy (in arbitrary units) vs. T behaves in a way typical of a soft mode (it tends to zero as T approaches T_{C}). At $T_1=150$ K the energy does not entirely tend to zero although exhibits a clear tendency of decreasing as T approaches T_1 from the region of lower temperatures (quasisoft mode).

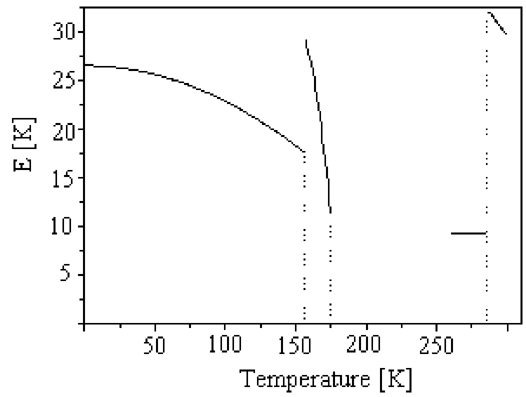

Figure 5. The energy of the bound lattice – active group vibrations as a function of temperature.

At $T_2=280$ K one observes only a jump in the energy. This obviously does not correspond to the behaviour typical of a soft mode.

The above facts indicate that at $T_{\mathrm{C}}=175$ K we really observe a structural phase transition. However, the anomalies observed at $T_1=150$ K and $T_2=280$ K cannot be classified as phase transitions.

Finally, we can conclude that the anomalous behaviour of the thermodynamic functions used in our analysis corresponds exactly to the singularities of the spectrum for collective excitations describing the system consisting of lattice vibrations and active dipole groups.

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Про зв'язок між даними ЕПР для SASeD легованого Cr^{3+} і м'якими модами

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Експериментальні результати досліджень SASeD легованого Cr^{3+} методами ЕПР подані з наголосом на виявлений вплив м'яких мод, а саме температурної залежності спін-гамільтонового параметра D_{ZZ} і ширини лінії ЕПР. Двопідґраткову модель, яка була запропонована і апробована раніше для SASD, узагальнено в напрямку врахування коливань ґратки. Отриманий спектр зв'язаних коливань системи підтверджує ідею про вклад м'яких мод у фазовий перехід при $T_c = 175$ К. Аномалія, виявлена при $T_1 = 150$ К має характер квазім'якої моди, а аномалію при $T_2 = 280$ К не можна віднести до ефекту м'яких мод.

Ключові слова: *натрій-амонієвий дигідрат селену, ЕПР, м'які моди, фазові переходи*

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