

RECENT RESULTS OF EPR AND MÖSSBAUER INVESTIGATIONS ON LATTICE DYNAMICS IN AMMONIUM SULPHATE

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1. INTRODUCTION.

Generally the ferroelectric transitions can be divided in to two major classes, depending on the microscopic mechanism which gives rise to spontaneous polarization of crystal - order-disorder transitions and displacive transitions. In order-disorder transitions, the permanent electric dipoles are present above the transition temperature and become ordered below that. In the displacive transitions the electric dipoles come into existence at the transition, when the unit-cell distorts in such a way that the dipoles are created. The process leading to such distortion of unit-cell can be explained by the cancellation of long-range Coulomb forces by short-range forces between ions. The cancellation of these forces leads to an anomaly in the frequencies of transverse optic TO vibrational mode. When $\vec{q} = 0$, the particular mode corresponds to entire Bravais lattice is moving as rigid units relative to each other.

Critical phenomena have received much attention in the last ten years, especially for the systems undergoing displacive phase transitions. Near the transition temperature the critical exponents of temperature dependencies for specific heat, susceptibility and order parameter are different from those predicted by Landau theory ($\alpha=0.$, $\gamma=1.$, $\beta=0.5$).

Ammonium sulfate (AS, hereafter) attracts interest by its complicated mechanism and salient dielectric properties, denoting complicated local dynamical changes, especially near transition temperature $T_c=223K$. Although AS belongs to A_2BX_4 family with β - K_2SeO_4 structure, it is the only member which undergoes a phase transition from the paraelectric $Pnam$ phase to the ferroelectric $Pna2_1$ phase, without passing through an incommensurate phase or changing the size of the unit cell [1]. Having two types of NH_4^+ ions it is of interest to know if the dynamics of these ions determines the phase transition at T_c . Many experimental techniques and theoretical studies have been used to explain the phase transition in AS, but the different explanations provided are at variance from each other, generally depending on the technique employed (with different time scales). The Mössbauer spectroscopy is the only technique missing till now in the series mention in [2]. In the paper we report on new evidence for the lattice dynamics, soft mode existence and critical anomalies near T_c by using new EPR and Mössbauer results in doped AS.

2. EXPERIMENTAL ASPECTS

The EPR and Mössbauer measurements have been carried out on crystals grown at room temperature, by slow evaporation of a saturated acidic aqueous solution of $(NH_4)_2SO_4$ to which small amounts of $HgCl_2$ (0.5at%), $VOSO_4$ (0.5at%) or $^{57}Fe_2(SO_4)_3$ (1at%). The glycerin was added to improve the crystal quality and habit. So, s-electron ion Hg^+ , polar ion VO^{2+} , and Mössbauer isotope ^{57}Fe were used to monitor the phase transition of AS. Two distinct sites, for each type of probe-ion with slightly different EPR parameters (g-factor, hyperfine constant) and Mössbauer parameters (central shift, quadrupole splitting, f-factor) have been identified and attributed to the two NH_4^+ positions of AS. It is worth noting that the spin-probes distribution into these sites is unequal and a preference for the site II was

observed. Different temperature behaviors were put in evidence upon passing the phase transition, depending on the nature and position occupied by each spin-probe.

2. ANOMALOUS TEMPERATURE DEPENDENCE OF SOME CHARACTERISTIC SPECTRAL PARAMETERS

2.1 HYPERFINE INTERACTION OF Hg⁺ ION.

S-electron ions, such as Hg⁺, with $(ns)^1$ configuration show characteristic EPR spectra due to very large hyperfine interactions and small anisotropy [3]. As they are very sensitive to ligand ion nature and on their dynamics, the s-electron ions could be successfully used in the critical phenomena studies of phase transitions. The EPR spectra of Hg⁺ ion in SA have been interpreted with the spin Hamiltonian:

$$\mathfrak{H} = \beta \cdot \vec{B} \cdot \underline{g} \cdot \vec{S} + \vec{S} \cdot \underline{A} \cdot \vec{I} - g_n \beta_n \cdot \vec{B} \cdot \vec{I} + \vec{I} \cdot \underline{Q} \cdot \vec{I} \quad (1)$$

where, the different terms have usual meanings. The Hg⁺ ion has two non zero nuclear spin isotopes (¹⁹⁹Hg, I=1/2 and ²⁰¹Hg, I=3/2). A perturbative procedure was developed in order to calculate the energy levels and the corresponding transitions; analytical solutions were obtained. EPR parameters have been calculated from the angular dependence of the EPR spectra, and two distinct centers were observed, corresponding to the NH₄⁺ substituted sites (I and II). The values of isotropic parameters are: $g=1.9955 \pm 0.0005$, $A=34065 \pm 10$ MHz (site I) and $g=1.9950 \pm 0.0005$, $A=34011 \pm 10$ MHz (site II). It is worth mentioning that for some values of $A/h\nu$, the NMR-type transitions in X-band are very sensitive on the value of hyperfine interaction, making possible its determination with a very high accuracy.

The relevant data for our study is the unusual temperature dependence of the isotropic hyperfine constant of Hg⁺ ion in SA. An anomalous temperature dependence superimposed on the normal one is observed for site I (Figure 1). This anomalous part is attributed to the existence of a soft mode [4] strongly coupled with the spin-probe in this position. Admitting that the temperature dependence is due to the mixing of higher lying orbital into the ground orbital through the orbit-lattice interaction, one can write

$$A(T) = A_0 - A_1 \cdot T + A_{an}(T) \quad (2)$$

where, the first two terms are determined by the normal vibration modes (in the $T \ll \theta_D$ approximation; θ_D -Debye temperature). The last term is singular and related to the lattice instabilities at the phase transition. They are induced by a soft mode existence, whose dispersion relation is approximately given by:

$$v^2(q, T) = \alpha(T - T_c)^\gamma + \beta(q - q_0)^2 \quad (3)$$

α and β are material constants and γ is the critical exponent ($\gamma=1$ in the mean field theory). The anomalous part $A_{an}(T)$, defined from the experimental data by subtracting the normal contribution, was fitted with

$$A_{an}(T) = -A_2 \cdot T \left(1 - \frac{\lim_{q \rightarrow 0} v(q, T)}{BQ} \arctan \frac{BQ}{\lim_{q \rightarrow 0} v(q, T)} \right) \quad (4)$$

using different γ values, in the range $|\Gamma - T_d| < 20$ K. B determines the dispersion of soft mode and Q the cut-off of the Brillouin zone. The best fit was obtained for the critical exponent $\gamma=1.24 \pm 0.03$, approaching the critical temperature $T_c=223 \pm 0.01$ K from below and $BQ=0.795 \pm 0.03$.

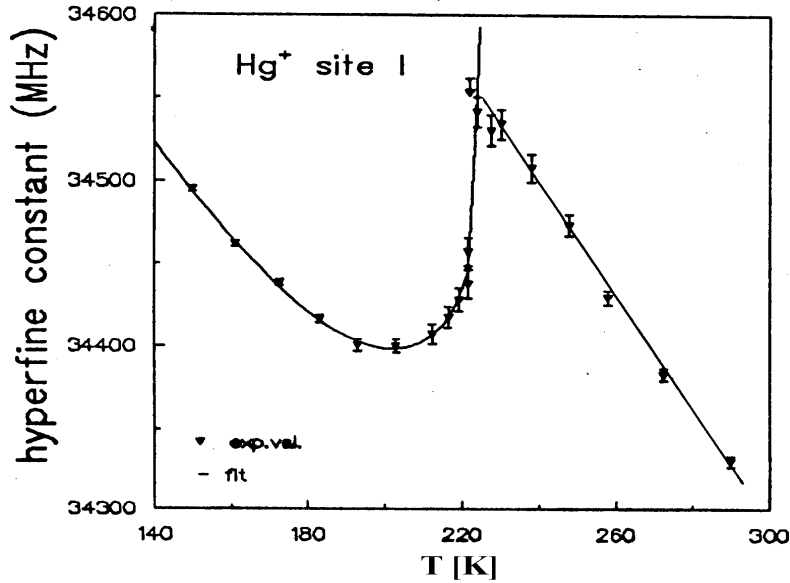


Fig. 1 Temperature dependence of the isotropic hyperfine constant of Hg^+ in SA

2.2 MÖSSBAUER FRACTION OF ^{57}Fe .

Two quadrupole doublets of Fe^{2+} ions, in nearly octahedral symmetry have been observed in $^{57}\text{Fe}:\text{SA}$ from Mössbauer experiments, conducted with a standard spectrometer in transmission geometry, operating in constant acceleration mode. The positions, widths, and intensities of the doublets have been carefully extracted by a least-squares adjustment of appropriate linear combinations of Lorentzians. Numerical calculations of the spectral Mössbauer parameters (central shift, integrated and normalized spectral area, quadrupole splitting) and of the ^{57}Fe electric field gradient tensors (calculated as a summation of crystalline lattice and valence electron contributions) have confirmed the Fe^{2+} probe in the ammonium sites [5]. Distinct effects are seen upon passing the phase transition. The spectral transition temperature $T'=229\text{K}$ does not coincide with T_c . The five degrees shift in the transition temperature, monitored by sudden changes observed in the experimental spectral parameters (central shift and integrated spectrum area) is likely due to the pinning effect of the ^{57}Fe impurity. Such shifts have been observed before in the literature, but usually for higher concentration of impurities [6].

The most sensitive experimental Mössbauer parameters on crystal lattice dynamics are the normalized integrated area a , and the relative central shift δ_c . These are linked to Mössbauer (or recoilless) fraction $f(T)$ and to the second order Doppler shift $\delta_{\text{SODS}}(T)$, as in

$$a = \chi \frac{\pi}{2} n \sigma_o f \Gamma; \delta_c = \delta_{is} + \delta_{\text{SODS}} \quad (5)$$

Here Γ , σ_o and n are the resonance half-linewidth, nuclear resonant cross-section, and the number of ^{57}Fe nuclei per unit area of absorber, respectively; the term δ_{is} is the isomer shift of the absorber nucleus. The temperature dependence of the integrated area shows an anomalous reduction, most probably corresponding to temperature dependence of the Mössbauer fraction f undergoing through the phase transition. The temperature dependence of f is well described within the Debye approximation (5). If it postulates that one of the vibrational modes has an temperature dependence as predicted by Cochran, then the Mössbauer factor expression becomes:

$$f(T) = \begin{cases} f_n(\theta_F; T) = \exp\left\{-\frac{3E_R}{2k\theta_F}\left[1 + 4\left(\frac{T}{\theta_F}\right)^2 \int_0^{\frac{\theta_F}{T}} \frac{xdx}{e^x - 1}\right]\right\}; T < T_c \\ f_{an}(T) \cdot f_n(\theta_P; T) = \exp\left[-\frac{E_R \bar{e}_{an}^2}{h\nu} \operatorname{cth}\left(\frac{h\nu}{k_B T}\right)\right] \exp\left\{-\frac{3E_R}{2k\theta_P}\left[1 + 4\left(\frac{T}{\theta_P}\right)^2 \int_0^{\frac{\theta_P}{T}} \frac{xdx}{e^x - 1}\right]\right\}; T > T_c \end{cases} \quad (6)$$

The soft mode contribution to the para-ferroelectric phase transition of AS was introduced by the temperature dependence of the Einstein frequency $\nu(T)$, with a dispersion relation given by (3), when $q_0=0$. The \bar{e}_{an}^2 is a weight of anomalous vibrational mode and θ_F , θ_P are the Debye temperatures in the ferroelectric and paraelectric phase, respectively. As one can see for the second-order ferroelectric transition $T_0=T_c$, at $T=T_c$ Mössbauer factor goes to zero and for the first-order transition $T_0 \neq T_c$, $T-T_0=T-T_c+T_c-T_0$, $f(T)$ goes to a nonzero minimum. Many parameters are needed to determine $f(T)$. So, the instability of one of the vibrational mode in the paraelectric phase of crystal can be detected by the spectral parameter of area. The deductible minimum of $f(T)$ can be altered by the changes of Debye temperatures θ and material constant α . That is not unreasonable due to the distortion of the crystal structure when this changes from non-polar state to polar one. So α , θ , T_c and T_0 and also T_c , are unknown quantities. Another unknown quantity is the γ exponent. The ratio $f(T)/f(T_c)$ shown to be not sensitive to the weight of anomalous vibrational mode[5]. It was considered $T_c=T'$. The Debye temperature of the AS crystal in ferroelectric phase was deduced from the relation (7), [8]

$$\theta_D^F \cong \frac{16M'c^2}{9E_\gamma k_B} (\delta_{is} - \delta_c(0)) \sqrt{\frac{M'}{M} \cdot \frac{k}{k'}} \quad (7)$$

M , M' and k , k' are the mass of iron and ammonium molecular groups and the effective force constants, respectively (approximated to be equally). The value $\theta_D^F \approx (373 \pm 65)K$ has obtained from (7) and it is similar with that obtained from the fit of $f(T)/f(\theta_D^F, T')$, which gives $\theta_D^F \approx (400 \pm 50)K$, for $T'=229K$. In the figure 2 is given the best fit of ratio $f(T)/f(\theta_D^F, T')$.

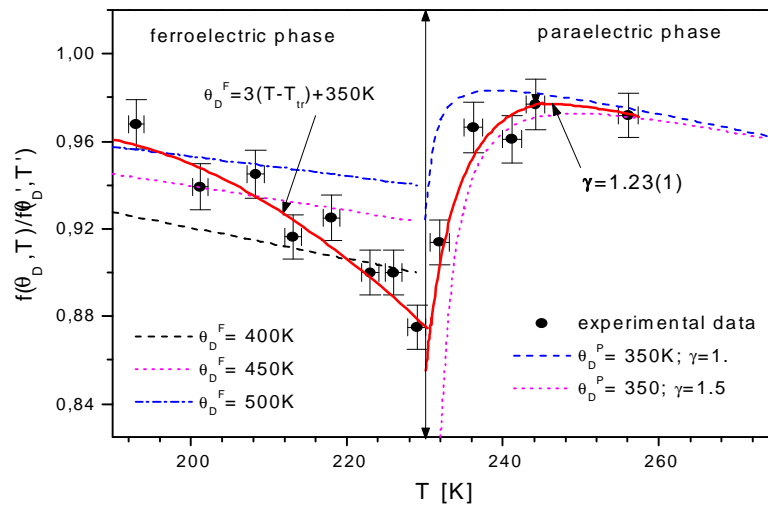


Fig. 2 The fit of experimental area fraction in the para- and ferroelectric phases of ^{57}Fe : SA

The anomalous reduction in f of about (12-13)% indicates that the Fe nuclei, substituting $\text{NH}_4(\text{I})$ and $\text{NH}_4(\text{II})$, are engaged in the soft-mode vibrations. It is remarkable that in the crystal with three or more interpenetrating Bravais lattices, it is possible that f may be unaffected by anomalous vibrational mode. If Mössbauer isotopes enter in one of lattices, Mössbauer factor will be sensitive only to the changes of that lattice. Two sublattices are necessary to evidence an instability of one TO -mode, $\nu \rightarrow 0$, if the Mössbauer nucleus is in the third, no anomaly of f and α may be shown at T_c . So, the presence of Mössbauer isotopes in the two-ammonium positions can explain the small value of the f anomaly at T_c . The critical exponent $\gamma=1.25\pm 0.15$ and the material constant $\alpha \approx 0.0105\text{eV}^2/\text{K}^\gamma$ which appear in the dispersion relation (3) of this soft vibration were obtained from the fit of the temperature dependence Mössbauer fraction in paraelectric phase. The best fit of $f(T)/f_n(\theta_D^P, T')$ was got with a Debye temperature $\theta_D^P=400\pm 75\text{K}$. These data are in agreement with the EPR ones although the time scales of the two measurements are quite different.

2.3 LINE SPLITTING OF VO^{2+} .

Because the critical exponent γ obtained from the above EPR and Mössbauer experiments is larger than unity, from the Rushbrooke relation [7] one should get a critical parameter $\beta < 0.5$. In order to verify this conclusion a careful EPR study of the polar VO^{2+} ion in SA was undertaken. Two main centers were observed in this case, corresponding to the substitution sites NH_4 -I and NH_4 -II of SA. Below T_c the lines split into a doublet, whose spacing increases with $T_c - T$. By applying of an external electric field the relative intensities were changed in the way expected from the hysteresis curve. Therefore one can conclude that this splitting is closely connected with a local electric field produced by the polarized domains. So, a temperature dependence of the form $(T_c - T)^\beta$ should be considered. By fitting it in the critical region $0 < T_c - T < 10$ K, for both centers, the following values were obtained for the critical parameter β , which define the temperature dependence of spontaneous polarization: $\beta=0.385$ for site I and $\beta=0.483$ for site II. These values are in excellent agreement with the corresponding γ values, which have been obtained from EPR and Mössbauer results. The probe in the site NH_4 -I seems to be more strongly coupled to the surrounding SO_4^{2-} .

3. CONCLUSIONS

In summary, anomalous temperature dependence of the EPR and Mössbauer spectra of AS doped with Hg^+ , ^{57}Fe and VO^{2+} ions have been observed, from which large isotropic hyperfine constants, crystal-field splittings, isomer shifts, Mössbauer fractions, and nuclear quadrupole couplings have been derived. These are explained in terms of the existence of vibration mode whose softening occurs due to local anharmonicity, having a significant contribution to the lattice dynamics. The critical exponents β and γ calculated in the critical region, confirm this hypothesis and are in agreement with the scaling and Rushbrooke relations for the paraelectric and ferroelectric phases, respectively.

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REFERENCES

- [1] H.Z. Cummins, *Phys. Rept.*, **185**, 212 (1990)
- [2] L.S. Smirnov, L.A. Shuvalov, I. Natkaniec, M.L. Martinez Sarrion, L. Mestres, *J. Korean Phys. Soc.* **32**, S98 (1998)
- [3] M.N. Grecu, *Rev. Roum. Phys.* **36**, 875 (1991)
- [4] H.G. Unruh, *Ferroelectrics*, **183**, 1 (1996)
- [5] S. Constantinescu, M.N. Grecu, *Balkan Phys. Lett. Supl.*, **5**, 1017 (1997)
- [6] M.L. Martinez Sarion, A. Rodriguez, L. Mestres, D. Ventura, *Ferroelectrics*, **166**, 3 (1995)
- [7] S.K. Misra, J. Sun, J. Jerzak, *Phys Rev.*, **B40**, 74 (1989)
- [8] S.Constantinescu, M.N. Grecu, *Rom. Journ. of Phys.* , **44**, 5-6, 585 (1999)