

PARAMAGNETIC RESONANCE OF Mn^{2+} IN KNO_3 SINGLE CRYSTAL: MOTIONAL EFFECTS

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ABSTRACT

The electron paramagnetic resonance of Mn^{2+} in KNO_3 single crystal is investigated over a temperature cycle through transition temperatures. The hyperfine coupling constant, A , half width, ΔH , and the line intensity, I , are found to show sudden changes at the transition temperature, at which α - KNO_3 changes into β - KNO_3 . The lines are much sharper in the high temperature β -phase than in α -phase of the crystal. They are explained, qualitatively, in terms of structure change and rotation of NO_3^- ions. The spectra in the two phases, α and β , are analysed in terms of usual spin-Hamiltonian. A search of metastable γ -phase is also made and probable indications for the same are found.

INTRODUCTION

Potassium nitrate has aragonite structure D_{2h}^{16} at room temperature (phase α) and is reported¹ to have the calcite structure D_{3d}^6 above $128^\circ C$. (Phase β). A number of interesting investigations have been made concerning the phase transformation of this substance²⁻⁴ and the metastable phase- γ which appears between the phases β and α , only on cooling (Fig. 1) has been found to be

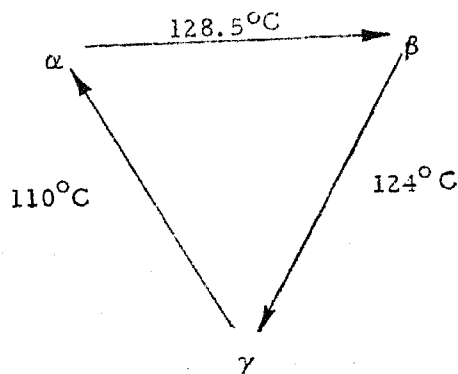


FIG. 1. Phase transformation of KNO_3 .

ferroelectric.⁵ Appearance of γ -phase depends also on previous heat treatment of the crystal and the water content of the same. Except for some radiation damage work,⁶ the crystal is untouched from the point of electron paramagnetic resonance. It was felt that a study of the electron paramagnetic resonance of doped KNO_3 would be useful to investigate not only the phase transformation but also the motional and exchange effects. We present here results obtained by such an investigation on Mn^{2+} ion in this crystal using a Varian model V-4502 EPR spectrometer along with model 4531 multi-purpose cavity. Line widths, line intensities and the hyperfine coupling constant are measured over a temperature cycle through the transition temperatures of phase transformation. The results are discussed in terms of structure change and motional effects.

THEORY

The electron paramagnetic resonance of Mn^{2+} ion in α - KNO_3 is analysed in terms of parameters of spin-Hamiltonian⁷

$$H = g \beta H.S + A I_z S_z + B (I_x S_x + I_y S_y)$$

and in the β -phase in terms of parameters of spin-Hamiltonian

$$H = g \beta H.S + A I_z S_z + B (I_x S_x + I_y S_y) + D [S_z^2 - \frac{1}{3} S(S+1)]$$

Line widths and line intensities are measured in the usual way by measuring the peak to peak separation in the dispersion curve and the area under the same respectively.

RESULTS

The electron spin resonance of Mn^{2+} ion in α - KNO_3 at room temperature shows only $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ transitions with six hyperfine lines with half width of approximately 42 gauss. As the temperature is increased, the hyperfine coupling constant, A , decreases, the intensities go down and the line widths increase, till at 118°C . when the spectrum is badly smeared. At 122°C . the sharp lines are seen superimposed on the smeared spectrum. At 124°C . the smeared spectrum disappears and the sharp spectrum becomes clear and shows a little fine structure splitting. These spectra are shown in Fig. 2. The fine structure parameters are very small though large enough to cause resolution. The hyperfine coupling is much smaller in the spectrum of the β -phase of the crystal as compared to the one of the α -phase at room temperature. Figure 3 shows the variation of line width (peak-peak) and line intensity (area under the dispersion curve) for a particular transition.

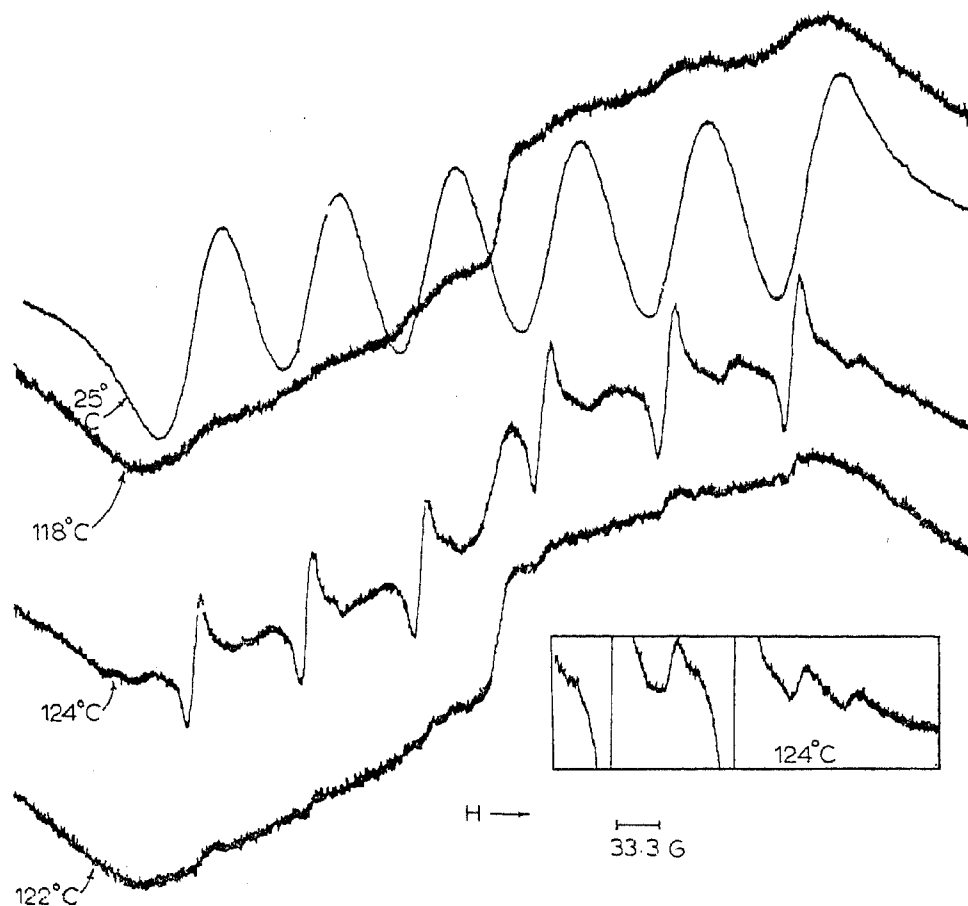


FIG. 2. Paramagnetic resonance spectra of Mn^{2+} in KNO_3 at $25^\circ C$, $118^\circ C$, $122^\circ C$ and $124^\circ C$. The insert shows high field side of the spectrum at $124^\circ C$, where some partial fine structure resolution is seen.

These variations are similar for all the transitions. Figure 4 shows the variation of hyperfine coupling constant with temperature. It is to be noted that maximum probable errors in the estimation of line widths and intensities are approximately 2 per cent in the range $25^\circ-90^\circ C$, 7 per cent in the range $90^\circ-118^\circ C$, and 0.5 per cent above $124^\circ C$. The hyperfine coupling constant is about one per cent. uncertain in the range $25-90^\circ C$., 1.5 per cent in the range $90-118^\circ C$, and about 0.1 per cent above $124^\circ C$. However, the abrupt change in these parameters as the crystal goes through the phase transformation is quite impressive. The spin-Hamiltonian parameters as obtained from the analyses in the two phases of the crystal are given in Table I. It is known that the metastable γ -phase of KNO_3 is obtained only on cooling particularly in crystals grown from melts.⁸ This phase is reported not to appear if the crystal contains water molecules. The crystals used in the present work were prepared from solutions. A careful search of the γ -phase

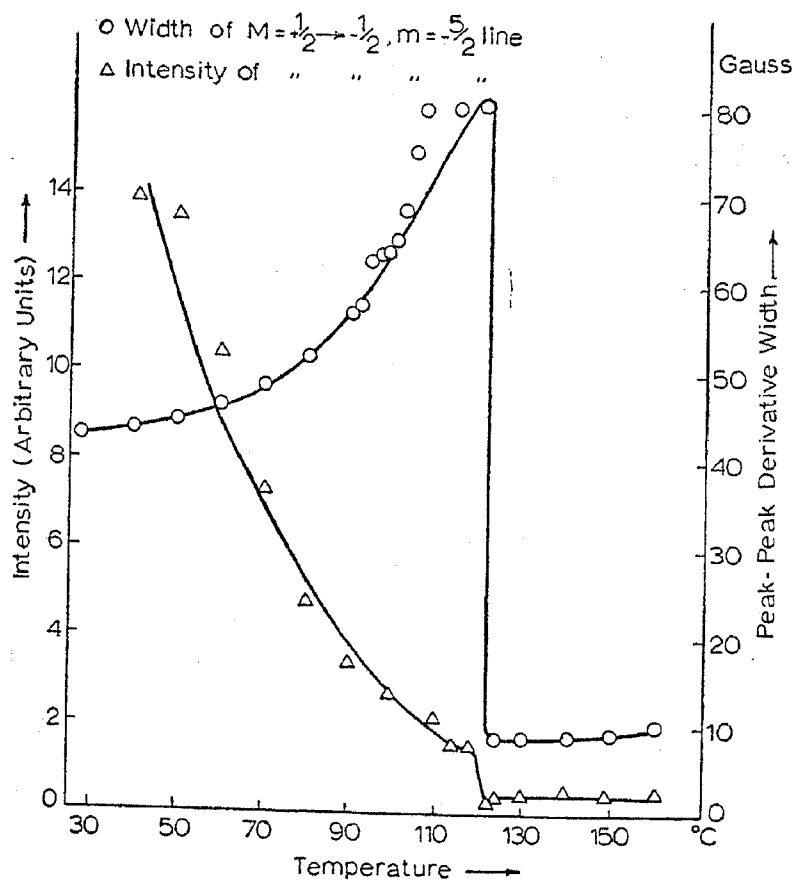


FIG. 3. Variation of line width and line intensities of $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$, $m = -5/2$ transition, with temperature, of the EPR spectrum of Mn^{2+} in KNO_3 single crystal.

was made in the present experiments. The crystal after being heated up to $160^\circ C$ was cooled slowly and resonance spectra were recorded in a suitable step of temperature. The spectra up to $124^\circ C$ were practically the same as those obtained while heating the crystal. However, they were slightly different below $124^\circ C$. The intensity of the spectrum dropped slowly as the crystal was cooled below $124^\circ C$ (Fig. 5 a-c), till at about $104^\circ C$ when the intensity was practically zero. Below $104^\circ C$ only a single line remained which persisted on further cooling.

DISCUSSIONS

The α -phase of KNO_3 consists of K^+ ions separated by double layers of NO_3^- ions. The latter are arranged antipolar along the b -axis and cannot make a whole rotation about any axis. Above the transition temperature, in the β -phase, on the other hand, the double layers of NO_3^- coalesce into a single one, and this change is probably favourable for the rotation of NO_3^-

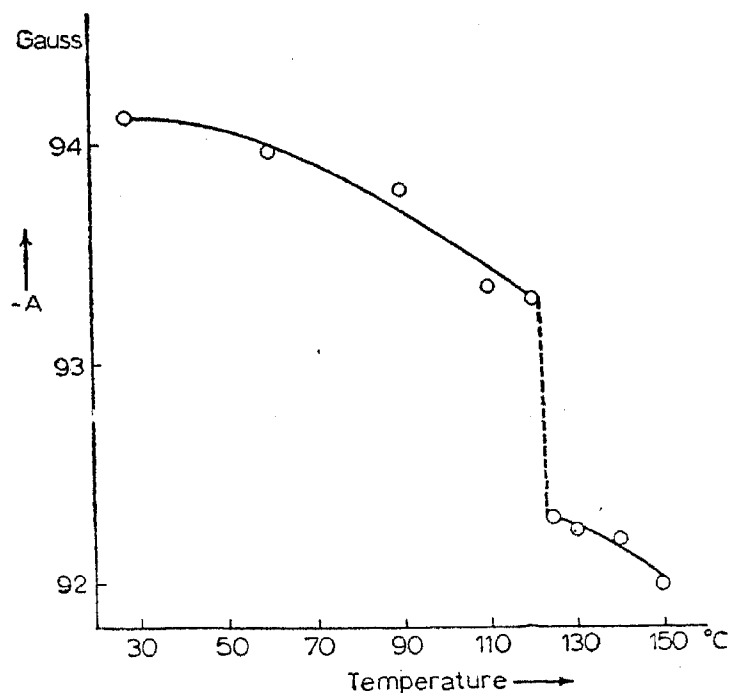


FIG. 4. Variation of hyperfine coupling constant of Mn^{2+} in KNO_3 single crystal as a function of temperature as the crystal passes through $\alpha \rightarrow \beta$ -phase transition.

TABLE I

Spin-Hamiltonian parameters of Mn^{2+} in α - and β - KNO_3

Phase	Temperature,	g	A	B	D
			$\times 10^{-4} \text{ cm.}^{-1}$	$\times 10^{-4} \text{ cm.}^{-1}$	$\times 10^{-4} \text{ cm.}^{-1}$
α	25° C.	2.0010 ± 0.002	87.9	86.8	..
β	130° C.	2.0016 ± 0.002	86.1	85.2	~ 24

groups. Tahvonen's X-ray measurements lead to the conclusion that in this form the nitrate groups are rotating about the trigonal axis and the rotation is connected with oscillations in the directions of this axis. It appears that this rotation of NO_3 groups in the β -phase is probably responsible to the sharpness of the lines in that phase. Another important reason for the sharpening of lines in the β -phase of the crystal is the fine structure resolution. The fine structure is not resolved in α -phase while it is partially resolved in

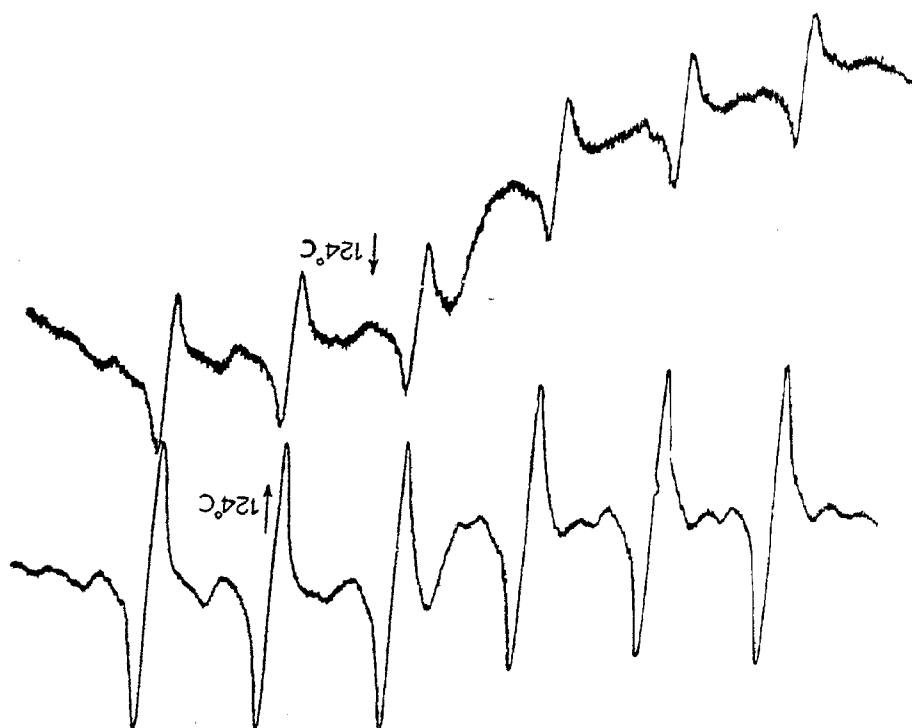


FIG. 5. (a) EPR spectra of Mn^{2+} in KNO_3 at $124^\circ C$ while heating (\uparrow) and while cooling (\downarrow) the crystal.

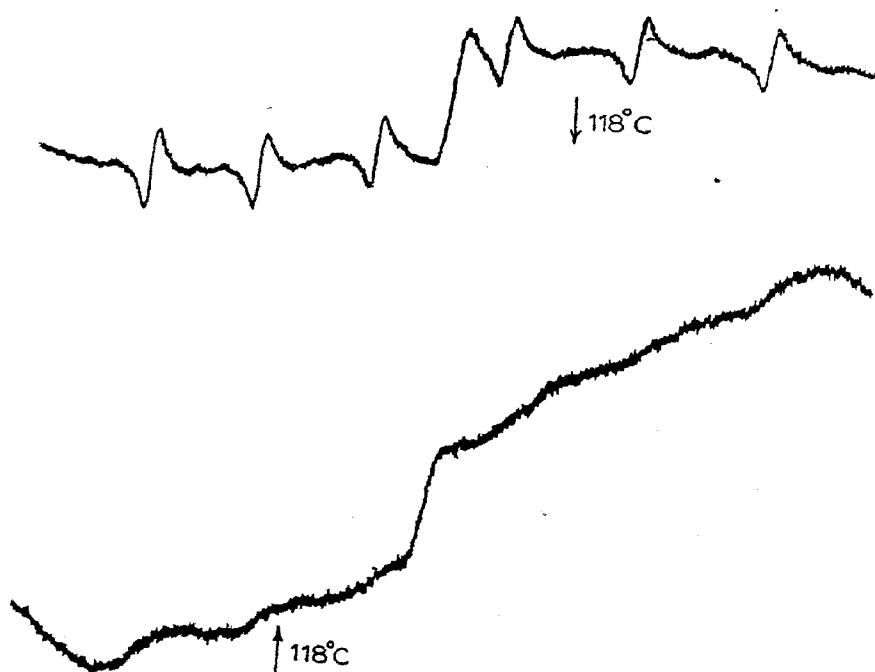


FIG. 5. (b) EPR spectra of Mn^{2+} in KNO_3 at $118^\circ C$ while heating (\uparrow) and while cooling (\downarrow) the crystal.

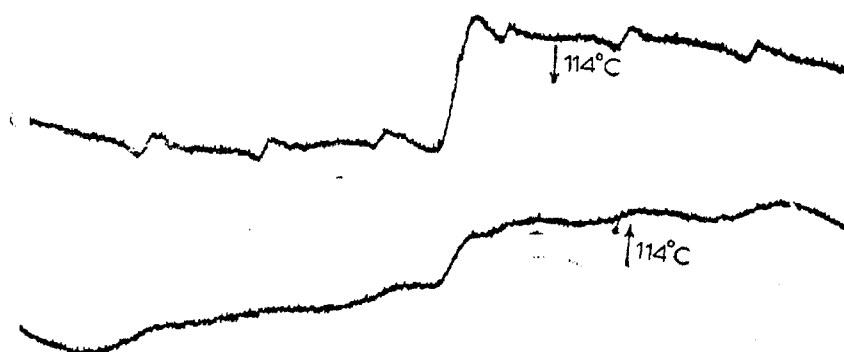


FIG. 5. (c) EPR spectra of Mn^{2+} in KNO_3 at $114^\circ C$ while heating (\uparrow) and while cooling (\downarrow) the crystal.

the β -phase. The intensity variations probably come from the thermal redistribution of populations.

Since the hyperfine coupling constant is approximately given by $2\beta\beta_n\gamma\langle r^{-3}\rangle$ we conclude that the change in it is due to a change in $\langle r^{-3}\rangle$ which comes from the change in structure of the crystal.

It may be mentioned that we observed the $\alpha \rightarrow \beta$ -phase transition approximately at $122^\circ C$ contrary to that at $128.5^\circ C$. as observed earlier in pure potassium nitrate. This is probably due to presence of Mn^{2+} ion impurity, since the transition temperature is known⁹ to be affected by the presence of impurities. Further, the presence of two types of spectra at $122^\circ C$ demonstrates the co-existence of phases in a very narrow range of temperature.

When the crystal was cooled, the spectra below $124^\circ C$ were slightly different from those obtained while heating the crystal. It is not clear whether this slight difference is due to the appearance of the γ -phase or due to hysteresis reasons. The intensity of the sextet was practically zero below $104^\circ C$ where a single line remained. The origin of this single line is still to be looked into.

ACKNOWLEDGEMENT

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