

## Universal scaling law for first order phase transformation: $\text{LiKSO}_4$

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**Abstract.** We have measured the kinetics of phase transition in  $\text{LiKSO}_4$  ( $C_6^6 \rightarrow C_{3v}^4$ ;  $T_c \sim 201$  K) by monitoring the time-dependent change in Raman intensity of selected vibrational lines at various temperatures in the transformed phase  $C_{3v}^4$ . We find that the observed growth curves for several temperatures display a nearly universal shape when plotted against a suitably scaled time parameter. We interpret our results in terms of a phenomenological model of nucleation and growth.

**Keywords.** Phase transition; first order; kinetics; scaling.

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### 1. Introduction

Phenomenological theories of kinetics of phase change in crystals involving nucleation and growth processes appeared in the literature more than forty years ago (Avrami 1939; Turnbull 1956). In the modern understanding of these phenomena, a key concept is that of scaling behaviour which implies a universal shape for growth curves. A recent neutron scattering study at room temperature of the evolution of the pressure induced first-order phase transformation of RbI shows that the growth curves for the various pressures indeed display a nearly universal shape when plotted against a scaled time parameter (Yamada *et al* 1984; Hamaya *et al* 1986). However, there have not been many investigations to verify the applicability of the scaling hypothesis to reconstructive structural first-order phase transitions which occur for a large number of crystals. We have used the Raman scattering technique to probe the kinetics of phase transition in  $\text{LiKSO}_4$  which we report here.

### 2. Experimental results

From a temperature-dependent Raman intensity measurements of polar modes of vibration of sulphate ions, it has been established by Bansal *et al* (1980) that  $\text{LiKSO}_4$  undergoes a first order phase change ( $C_6^6$  to  $C_{3v}^4$ ) when the crystal is cooled below  $T_c \sim 201$  K. The transition was also found to be sluggish. These findings were subsequently confirmed by neutron diffraction (Sandhya *et al* 1985) and ESR studies (Maezawa *et al* 1985; Sastry *et al* 1987).

As shown in an earlier paper (Bansal *et al* 1980), for the  $\nu_3$  ( $\text{SO}_4$ ) internal vibration occurring at  $1202 \text{ cm}^{-1}$ , the Raman intensity corresponding to the  $xy$  component is symmetry forbidden in the  $C_6^6$  phase and symmetry allowed in the  $C_{3v}^4$  phase. In the

present investigation, the time-dependent intensity of the above line was recorded after sudden cooling of the crystal from  $T > T_c$  to  $T < T_c$ . This directly gives information about the fraction of the sample transformed,  $X(t)$  as a function of time  $t$ . Intensity plots as a function of time at different temperatures are shown in figure 1. These were recorded using a spectral bandpass of  $3.5 \text{ cm}^{-1}$ . Two of the spectra exhibit slight decrease in intensity after reaching maximum (figure 1). This could be attributed partly to drift in laser power and spectrometer settings. The experimental arrangement was very similar to the one employed earlier. For details about the laser Raman spectrometer, see Roy and Bansal (1988).

It is known from previous work (Bansal and Roy 1984) that this phase transition in  $\text{LiKSO}_4$  is associated with cooperative reorientation of one of the sulphate ions in the unit cell. The dynamical processes occurring during phase transition give rise to an initial build-up and subsequent decay of Raman intensity  $I_{zy}$  corresponding to the  $\nu_1(\text{SO}_4)$  mode at  $1012 \text{ cm}^{-1}$  in the  $y(z)y_x$  configuration. The  $\nu_1$  mode does not have any off-diagonal Raman tensor component for both the phases once the equilibrium has been reached. The observed intensity is a measure of the rate of transformation from  $C_6^6$  phase to  $C_{3v}^4$  phase (figure 2). In the above experiment the crystal temperature was kept just below  $T_c$ ; it takes typically 40 min for the phase transformation to be completed at this temperature. Time dependence of the fractional volume of transformed region  $X(t)$  can be simply deduced from figure 2 by computing the area of the experimental curve upto the time  $t$ . Thus an independent estimate of  $X(t)$  vs  $t$  is obtained which can be compared with the results presented in figure 1. In order to do this, we define at each temperature a characteristic scaling time  $\tau_{1/2}(T)$  for the transformation through the relation  $X(\tau_{1/2}) = 0.5$ . When plotted (figure 3) using a scaled time parameter  $t/\tau_{1/2}(T)$ , we get the remarkable result that  $X(T, t)$  displays a nearly universal shape over a range of temperatures.

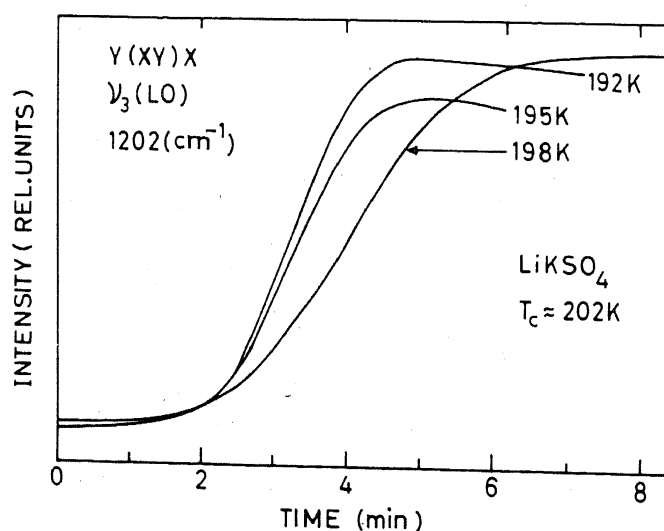


Figure 1. Time dependence of intensity of the  $\nu_3$  line in the transformed phase  $C_{3v}^4$  at various temperatures.

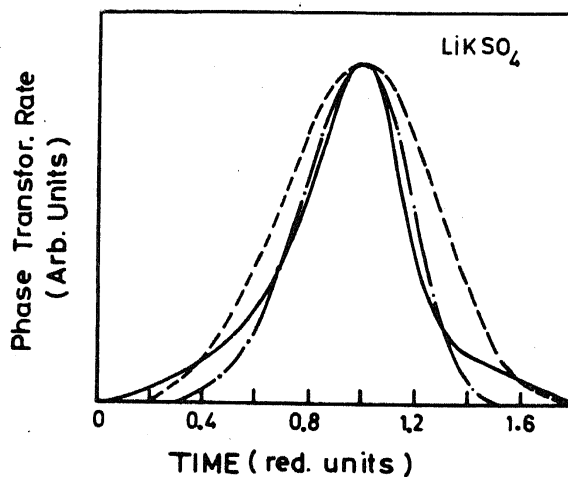


Figure 2. The solid line represents time dependence of intensity of the  $\nu_1$  line at  $1012 \text{ cm}^{-1}$  in an off-diagonal geometry  $I_{zy}$  during phase transformation. The crystal temperature is maintained just below  $T_c$ ,  $|T - T_c| \sim 0.5^\circ\text{K}$ .  $dX/dt$  calculated from equations (3) are also shown for  $n = 4$  (---) and  $n = 5.3$  (-·-·-).

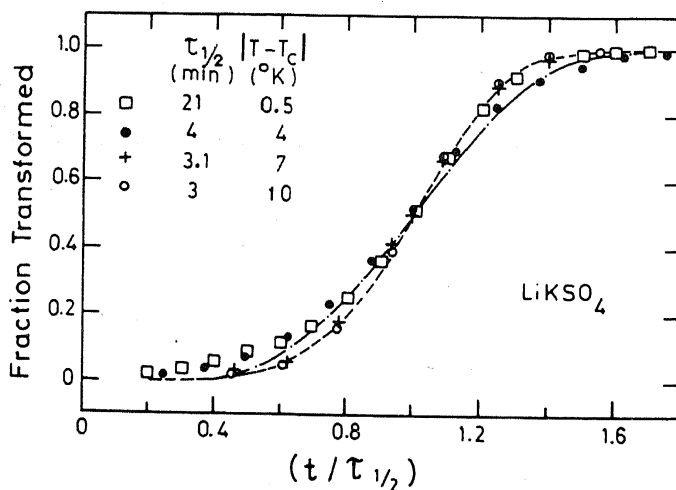


Figure 3. The experimental data for  $X(t)$  are plotted in terms of scaled time  $(t/\tau_{1/2})$  at various temperatures. The theoretical curves calculated from equation (3) are shown for  $n = 4$  (---) and  $n = 5.3$  (-·-·-).

### 3. Analysis

Phenomenological theories for the kinetics of phase change across a first order transition ( $\alpha \rightarrow \beta$ ) have been developed (Turnbull 1956; Raghavan 1987). It is assumed that the rate of phase change  $dX/dT$ , where  $X$  is the fraction of  $\alpha$  transformed isothermally to  $\beta$  in time  $t$ , is determined by two constants: the rate of nucleation  $s$  of domains and the domain wall velocity  $u$  after nucleation. If we take  $s$  and  $u$  to be time-independent, then for polyhedral growth i.e. assuming that domains grow into pseudospherical shape, one arrives at the kinetic law:

$$X(t) = 1 - \exp(-(\pi/3) \cdot su^3 t^4). \quad (1)$$

By defining a scaled time variable  $\tau = t/t_0$  with  $t_0 = (\pi s u^3/3)^{-1/4}$ , we find the universal relation

$$X(\tau) = 1 - \exp(-\tau^4). \quad (2)$$

More generally when  $s$  is time-dependent, the kinetic growth law can be expressed as

$$X(\tau) = 1 - \exp(-\tau^n). \quad (3)$$

If there is a volume difference between the two structures  $\alpha$  and  $\beta$ , then the domain wall growth rate  $u$  may also become time-dependent because of the presence of elastic strain (Hamaya *et al* 1986). However, for  $\text{LiKSO}_4$  there is no measurable change of volume (Sharma 1979) in the temperature range relevant to the present investigation.

The comparison of our experimental results with the model calculation for  $n = 4$  (equation (2)) is shown in figure 3. Though a general agreement with the experimental data is seen, a more sensitive test is provided by comparing with the rate of phase transformation ( $dX/dt$ ) curve presented in figure 2. This brings out clearly the discrepancy between the computed and experimental curves. A better fit is obtained when  $dX/dt$  is calculated from (3) taking  $n = 5.3$ . To facilitate comparison appropriate time scales have been chosen such that the experimental and the theoretical curves all peak at 1.0 in reduced units of time.  $X(t)$  computed using the value  $n = 5.3$  is also plotted in figure 3. In (3),  $n > 4$  implies that the nucleation rate increases with time (Raghavan 1987). It has, of course, been recognized in the literature (Turnbull 1956) that the value of kinetic law exponent  $n$  alone is not adequate to establish the growth habit of a precipitate. Various factors may modify the form of the kinetic law. For example, one may consider the possibility of finite critical droplet size  $r_c$  (Ishibashi and Takagi 1971). The nuclei redissolve or grow according to whether their radius is greater or less than  $r_c$ . We have thus far implicitly assumed  $r_c = 0$ . Equation (2) can be suitably modified to take into account finite  $r_c$ . It is possible to obtain better agreement with experimental data; however since the formulation now requires two characteristic times,  $X(t)$  is no longer universal.

#### 4. Summary and conclusions

The kinetics of phase transition in  $\text{LiKSO}_4$  has been investigated by measuring the evolution of Raman intensity of vibrational modes as a function of time for various temperatures in the transformed phase. We were also able to probe directly the dynamical fluctuations occurring during phase transformation associated with reorientation of sulphate ions about an axis normal to the  $c$ -axis of the crystal. Our results suggest that the observed growth curves for several temperatures display a nearly universal shape when plotted against a suitably scaled time parameter. This is shown to be in accordance with predictions of simple models of nucleation and growth.

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