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^{29}Si magic-angle-spinning NMR spectroscopy of the ferroelastic-to-incommensurate transition in Sr_2SiO_4

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The soliton density of the incommensurate α'_L phase of Sr_2SiO_4 has been determined by ^{29}Si magic-angle-spinning NMR spectroscopy from $T_c = 83\,^\circ\mathrm{C}$ to $200\,^\circ\mathrm{C}$. On heating, the soliton density increases rapidly from 0.06 at 83 °C to 0.6 at 86 °C but then increases only gradually to 0.76 at 200 °C. On cooling through the transition, there is a 10° thermal hysteresis and the decrease in soliton density with temperature is more gradual than on heating. The temperature dependence of the soliton density is similar to that for the A_2BX_4 class of improper ferroelectrics such as Rb_2ZnCl_4, although the commensurate phase of Sr_2SiO_4 is ferroelastic rather than ferroelectric. In addition, the modulation wave appears to be pinned over this temperature range.

INTRODUCTION

Sr_2SiO_4 undergoes a series of structural phase transitions with changing temperature from an ordered ferroelastic form (β) at low temperature to the high-temperature disordered α'_H form via the incommensurately modulated α'_L phase:[1,2]

$$\beta \overset{T_c}{\leftrightarrow} \alpha'_L \overset{T_i}{\leftrightarrow} \alpha'_H \; .$$

The $\beta \rightleftarrows \alpha'_L$ transition occurs at $T_c \approx 90\,^\circ\mathrm{C}$ and the $\alpha'_L \rightleftarrows \alpha'_H$ transition occurs at $T_i \approx 500\,^\circ\mathrm{C}$. Morphological evidence suggests that there is a third, higher-temperature transition to a hexagonal α form with b^* parallel to the hexagonal c axis.[1]

The crystal structure of Sr_2SiO_4 has the topology of the β-K_2SO_4 structure, which is common among A_2BX_4 inorganic compounds.[3] Sr_2SiO_4 (and other alkaline-earth orthosilicates, such as Ca_2SiO_4) are isomorphous to the well-studied class of improper ferroelectrics which includes phases such as Rb_2ZnBr_4, Rb_2ZnCl_4, and K_2SeO_4 which undergo a similar set of transitions.[4,5] For Sr_2SiO_4, however, the low-temperature, ordered, β form is a pure ferroelastic which is polysynthetically twinned on (100).[2] The β phase ($P2_1/n$) is related to the parent α'_H phase ($Pmnb$) by a shearing of the structure which results in the loss of the σ_x.

The intervening incommensurate α'_L phase has been observed in electron-diffraction experiments by the appearance of two sets of satellite Bragg reflections with wave vectors $\mathbf{q}_1 = 0.303\mathbf{b}^*$ and $\mathbf{q}_2 = 0.396\mathbf{b}^*$, where $\mathbf{q}_2$ is a second harmonic of $\mathbf{q}_1$.[1] These wave vectors do not change with temperature through the α'_L phase.

Several interesting aspects of this series of transitions in Sr_2SiO_4 distinguish it from those that occur in the improper ferroelectrics mentioned above. (1) The incommensurate phase is stable over a wide temperature interval (≈400°). (2) The transitions occur at high temperatures compared to other β-K_2SO_4-type structures and thermal unpinning of the modulation wave may occur. (3) Although the modulation wave vector is nearly $\frac{1}{3}b^*$, the modulation wave locks in at the zone center and there is no integral multiplication of the unit cell from the disordered to ordered forms ($p = 1$).

Magnetic resonance techniques have played an important role in elucidating the characteristics of many structural phase transitions (SPT's) in solids[6] and have led to significant advances in the understanding of incommensurate phases in dielectrics.[7] The temperature dependence of NMR parameters can be used to determine the temperature evolution of the order parameter and the nucleus can serve as a local probe of the structure, under favorable circumstances providing a measure of the spatial variation of the phase of the modulation wave in incommensurate phases. EPR, NMR, and nuclear quadrupole resonance (NQR) techniques have been applied successfully in the study of the incommensurate phases of A_2BX_4-type compounds including Rb_2ZnCl_4, Rb_2ZnBr_4, and K_2SeO_4.[7-11]

Previous NMR studies of incommensurate phases have focused on the quadrupole-perturbed NMR spectra of quadrupolar nuclei in single crystals. The electric-field gradient at the nucleus can be probed through the coupling to the nuclear quadrupole moment which modifies the nuclear resonance frequency. The spectral density reflects the distribution of local configurations in the incommensurate phase and analysis of the resulting line shape can give the soliton density and amplitude of the modulation wave with temperature.[7] Such experiments are limited to single crystals because the orientation dependence of the frequency with respect to the polarizing field produces broad, uninformative resonances for polycrystalline samples.

In this paper we show that similar information about the modulation wave may be obtained from polycrystalline samples by using high-resolution magic-angle spinning (MAS) NMR spectroscopy. Sr_2SiO_4 contains no abundant magnetic nucleus other than ^{29}Si ($I=\frac{1}{2}$, 4% natural abundance). For ^{29}Si, the principal line-broadening interactions are homonuclear dipole-dipole coupling and the orientation-dependent chemical shift anisotropy. Each of these interactions is averaged by rapid sample rotation at the magic angle (MAS), leaving a single line at the isotropic shielding position for each inequivalent Si. Thus, Sr_2SiO_4 is ideally suited for study by ^{29}Si MAS NMR spectroscopy. The ^{29}Si isotropic chemical shift (normalized resonance frequency) of Sr_2SiO_4 shows a surprising sensitivity to the spatial variation of the phase of the modulation wave in the incommensurate α'_L phase which enables us to determine the temperature dependence of the soliton density.

EXPERIMENT

The Sr_2SiO_4 sample was prepared by heating a stoichiometric mixture of 95% ^{29}Si-enriched SiO_2 and SrO (95.1 mg total) plus 10% SrF_2 flux in a sealed Pt capsule at 1400 °C for 12 h. Guinier powder x-ray-diffraction photographs of an identical parallel synthesis of an unenriched sample gave sharp lines for Sr_2SiO_4.

^{29}Si MAS NMR measurements were performed at 71.5 MHz using a home built spectrometer based on a Nicolet 1280 data-acquisition system. The sample was spun at about 2.5 kHz using a probe manufactured by Doty Scientific (Columbia, SC). The sample temperature was varied by heating the N_2 spinning gas. The reported sample temperatures are those in the heater, about 2 cm from the sample, and the actual sample temperatures might be 1°–3° lower.

Approximately 50 mg of the ^{29}Si-enriched Sr_2SiO_4 was packed into the center of a 7-mm-o.d. rotor under a dry nitrogen atmosphere. The remainder of the rotor (approximately 500 mg total) was filled with powdered α-Al_2O_3.

An approximately $\pi/4$ flip angle of the spin system by a 5-μs rf pulse and a 60 s recycle delay between 80 and 100 repetitions were used to collect the spectra. The ^{29}Si spin-lattice relaxation time T_1 is approximately 200 s. Preliminary experiments on an unenriched sample showed no significant dependence of the experimental line shape on the length of the recycle delay. Each spectrum took approximately 1.5 h to accumulate.

The ^{29}Si resonance frequencies are reported as ppm shifts from the ^{29}Si resonance frequency of external tetramethylsilane (TMS; 1 ppm = 71.5 Hz). More positive shifts correspond to increasing frequency (right to left in the spectra). The data collected during extended runs are corrected for the mean instrument drift of -0.4 ppm/day (approximately -0.02 ppm per spectrum). The chemical shifts are reported to 0.01 ppm to retain accuracy through calculations, but the precision is only about ± 0.05 ppm due to changes in the homogeneity of the H_0 field with changing temperature and instrument drift over time.

RESULTS

The ^{29}Si: MAS NMR spectrum of β-Sr_2SiO_4 (Fig. 1) contains a single resonance at -69.42 ppm which is approximately Lorentzian in shape with a FWHH of 0.24 ppm. The peak for β-Sr_2SiO_4 shifts slightly to higher frequency with increasing temperature to -69.20 ppm at 80 °C.

The single, narrow resonance observed in β-Sr_2SiO_4 is consistent with the crystal structure for this phase, which contains one crystallographically inequivalent Si-position.[3] The small linewidth and long T_1 indicate a low concentration of other magnetic nuclei and paramagnetic impurities. The chemical shift of -69.4 ppm is similar to those reported by Grimmer *et al.*[12] for the structurally analogous polymorphs of Ca_2SiO_4.

At 83 °C, the transition to the α'_L phase is indicated by the appearance of a broad, asymmetrical doublet (Fig. 1). The less intense peak in the doublet is at -68.3 ppm, whereas the second peak occurs at about the same position as the peak from the β phase just below T_c. With increasing temperature the more intense peak shifts to higher frequency from -69.26 ppm at 83 °C to -69.08 at 200 °C, whereas the position of the less intense peak remains approximately constant at -68.3 ppm (Fig. 2). In addition, the relative intensity of high-frequency peak increases monotonically with increasing temperature.

The decrease in the sharpness of the spectrum on heating from room temperature (RT) to 100 °C is probably due to a decrease in the homogeneity of the H_0 field because similar changes occurred in the shape of the reso-

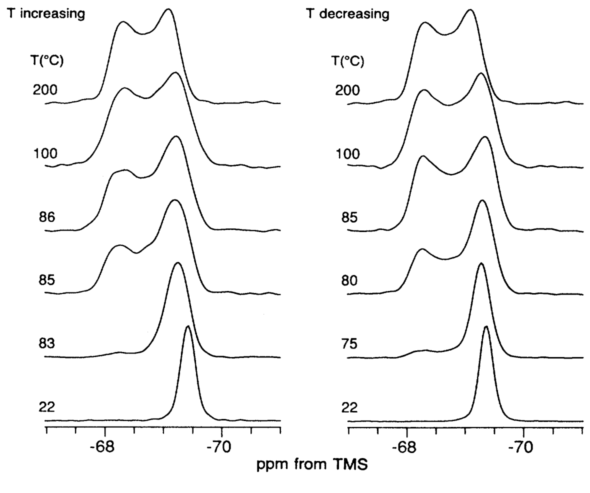

FIG. 1. ^{29}Si MAS NMR spectra of Sr_2SiO_4 with increasing temperature (°C) on the left-hand side and decreasing temperature on the right-hand side. On heating, the transition $\beta \rightarrow \alpha'_L$ occurs at about 83 °C, but upon cooling the lock-in transition $\alpha'_L \rightarrow \beta$ occurs below 70 °C.

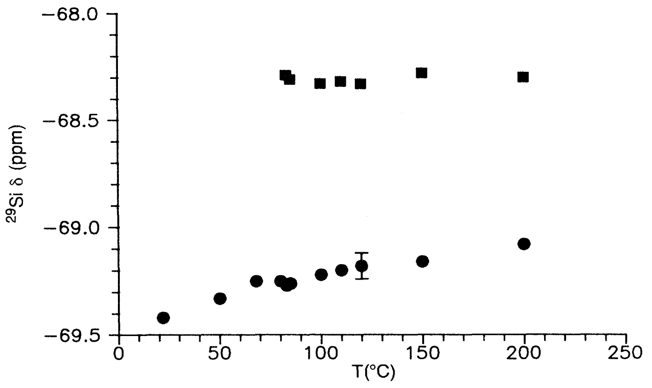

FIG. 2. Variation of the ^{29}Si NMR peak positions of Sr_2SiO_4 with increasing temperature. Position of the high-frequency peak, which appears at T_c on heating, remains approximately constant, whereas the low-frequency peak shifts to higher frequency with increasing T.

nance of an internal Mg_2SiO_4 standard.

With decreasing temperature from 200 °C most of the changes in the spectra are reversed through the transition. The doublet, however, persists upon decreasing temperature to below 70 °C, corresponding to a thermal hysteresis of at least 10°. Also, the separation between the two peaks increases with decreasing T to T_c (1.05 ppm at 85 °C), reversing the trend observed with increasing T, but then appears to decrease with further cooling below T_c to about 0.95 ppm. The relative intensity of the peak at −68.3 ppm, still present at 70 °C upon cooling, did not increase significantly when the temperature was raised again to 85 °C (near T_c).

The spectrum taken at 25 °C after completion of the experiments to 200 °C is not significantly different from the spectrum taken at the start of the experiment.

The broad doublet observed in the ^{29}Si NMR spectra of the α'_L phase resembles the EPR spectrum of the incommensurate phase of γ-irradiated K_2SeO_4 and is characteristic of an incommensurately modulated phase.[13,14] The incommensurate structural modulation observed by Withers *et al.*[1] in the α'_L phase by electron diffraction corresponds to a continuum of Si environments and thus a distribution of isotropic chemical shifts. The peak maxima in the spectra represent peaks in the spectral density of this distribution.

As described by Blinc *et al.*,[7,15] the ^{29}Si resonance frequency (δ) depends on the position of the Si-atom along the modulation wave [$\delta=\delta(x)$] and can be expanded in terms of the displacement, u. In the local approximation:

$$\delta(x)=\delta_0+\delta_2 u^2+\cdots \ . \tag{1}$$

The expansion in Eq. (1) contains only even-order terms as required by the point-group symmetry m of the Si position in the disordered paraelastic phase.[3] The local approximation should be valid because the changes in magnetic screening of the ^{29}Si nucleus are due principally to changes in the electronic configuration of the atom of interest, a distance much shorter than the wavelength of the modulation wave ($\approx 3b = 30$ Å).

We take the displacement u to be an even, periodic function of the phase of the modulation wave:

$$u = A\cos\phi(x) \ , \tag{2}$$

where A is the amplitude of the modulation wave and is taken to be constant as a first approximation. Combining Eqs. (1) and (2) gives, to second order,

$$\delta(x)=\delta_0+\delta'_2\cos^2[\phi(x)] \ , \tag{3}$$

where δ_2 (dropping the prime) is now proportional to the square of the amplitude.

Given the even-ordered expansion of Eq. (3), the asymmetrical ^{29}Si NMR lineshape observed for the incommensurate phase can occur if the spatial variation of the phase of the modulation wave is nonlinear.[14] This result is consistent with the presence of Bragg reflections from higher-order harmonics in the electron-diffraction patterns of the α'_L phase noted above.

A model for the spatial variation of the modulation wave may be obtained by solution of the sine-Gordon equation, which minimizes the free-energy density of the incommensurate phase with respect to the phase of the modulation wave.[16] To reduce computing time, we use an approximation for the multisoliton solution to the sine-Gordon equation:

$$\phi(x)=\sum_n 4/p \arctan\exp[a(x-nb)]+\phi_0 \ , \tag{4}$$

where π/a is the soliton width, b is the intersoliton spacing, and ϕ_0 is the initial phase of the modulation wave. ϕ_0 describes the relative position of the incommensurate continuum with respect to the commensurate-like regions. The variation in Eq. (4) can be described by a single parameter, the soliton density (n_s), which is a measure of the fraction of the crystal occupied by the domain walls and is simply the soliton width divided by the intersoliton spacing:

$$n_s=\frac{\pi}{ab} \ . \tag{5}$$

n_s can vary between 1 in the plane-wave limit and 0 for a commensurate structure and is the order parameter for the transition at T_c from the incommensurate phase to the low-temperature, ordered phase.

To calculate the ^{29}Si NMR line shapes, 500 chemical shifts were computed using Eqs. (3) and (4) at evenly spaced intervals spanning one period of the modulation wave. The resulting grid in frequency space was then convolved with a pseudo-Voight function (Lorentzian plus Gaussian) and normalized to unit integral. Computed line shapes were compared directly to the normalized observed spectra and the best-fit parameters obtained by minimizing χ^2 using a simplex algorithm to navigate through parameter space. Generally, there is a well-defined minimum in parameter space which is independent of reasonable initial guesses.

The simulations based on Eqs. (3) and (4) give very satisfactory results (Fig. 3). As a result, n_s (Fig. 4), δ_0, and

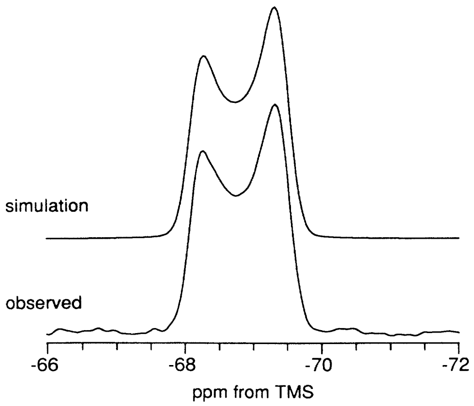

FIG. 3. Example of a least-squares fit of the ^{29}Si MAS NMR spectra of the incommensurate phase of Sr_2SiO_4 to Eqs. (3) and (4). The observed spectrum was obtained at 85 °C (decreasing temperature) and simulated with $n_s=0.69$, $\delta_0=-68.19$ ppm, and $\delta_2=-1.30$ ppm.

δ_2 can be determined as functions of temperature. For most of the spectra, fitted values of ϕ_0 vary insignificantly from 0, except near T_c where the intensity from the continuum is low and the uncertainty in the fitted parameters is proportionately larger. Near T_c, the effect of a small ϕ_0 (10° at most) is primarily to increase the fitted value of δ_2 relative to a fit for $\phi_0=0.0$, but to not significantly change the fitted value of n_s.

With increasing temperature, n_s increases rapidly from 0.06 at 83 °C to about 0.6 at 86 °C then levels off, increasing to only 0.76 by 200 °C. It is expected that in the high-temperature portion of the incommensurate phase, the modulation wave should approach the plane-wave limit ($n_s=1.0$). Clearly, the data extend only partially into the stability field of the α'_L phase, consistent with the previously observed temperature of the incommensurate to paraelastic transition at about $T_i \approx 500$ °C.[1]

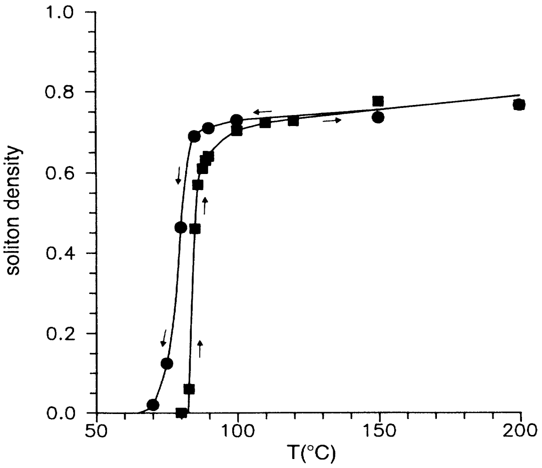

FIG. 4. Temperature dependence of the soliton density in incommensurate α'_L-Sr_2SiO_4, obtained from least-squares fits to the ^{29}Si NMR spectra. The squares denote increasing temperature and the circles denote decreasing temperature.

With decreasing temperature, n_s appears to remain nearly constant until 85 °C where it drops rapidly from 0.7 to 0.1 by 75 °C. Further decrease in n_s is gradual, with n_s still nonzero at 70 °C. This type of behavior is very similar to that observed for Rb_2ZnCl_4 (Refs. 9 and 10) and may be due to the formation of a metastable chaotic phase below T_c in which the intersoliton spacing is random.[17]

It should be noted that although these results were obtained using constant-amplitude approximation, Blinc *et al.*[18] have shown that amplitude fluctuations may be important in the incommensurate phase near T_c. Unfortunately, the resolution of our spectra do not justify the addition of more parameters to the line shape analysis. However, amplitude fluctuations may explain the apparent decrease in δ_2 (peak separation) observed with decreasing T below T_c.

The fitted values for δ_0 and δ_2 [Eq. (1)] show that δ_0 is independent of temperature. This result supports the use of the local approximation for the power series expansion in Eq. (1). δ_2, which is approximately equal to the splitting between the peaks (Fig. 2), decreases linearly to 200 °C. δ_2 is proportional to the square of the amplitude of the modulation wave [Eq. (3)], which is the order parameter for the incommensurate to paraelastic transition. From Landau theory, δ_2 should have a temperature dependence of the form

$$\delta_2=c\left[\frac{T_i-T}{T_i}\right]^{2\beta}, \tag{6}$$

where β is the critical exponent. A least-squares fit to Eq. (6) gives a value for $\beta=0.31$, which is also very similar to that observed for Rb_4ZnBr_4 and Rb_2ZnCl_4.[8,19] Although the fit is not well constrained because there are no data near T_i, the fitted value for $T_i=496$ °C is close to that observed by electron diffraction (≈ 500 °C).

In the high-temperature part of the incommensurate phase, the modulation wave may become unpinned, making the phase of the modulation wave both time and space dependent.[19] Such a thermal unpinning of the modulation wave symmetrically narrows the line shape but does not distort its shape. This motional narrowing results in a more rapid decrease of the frequency splitting of the singularities (δ_2) with temperature than predicted by Eq. (6). Up to 200 °C, the temperature evolution of δ_2 is described by a reasonable value for β and shows no break in slope in a log-log plot, indicating that the modulation wave is still pinned.

For $I=\frac{1}{2}$ nuclei, the isotropic chemical shift obtained from high-resolution MAS NMR experments can be used as a local probe of the spatial characteristics of incommensurate modulation waves in insulating materials. Although the ratio of the frequency splitting to inhomogeneous plus instrumental line broadening is not as large as for many quadrupolar nucleus in single crystals, the temperature dependence of the soliton density and amplitude can nevertheless be determined. This capability is important for phases, such as Sr_2SiO_4, which do not contain an abundant quadrupolar nucleus and/or cannot be grown as large single crystals and whose incommensurate wave vectors show no temperature dependence. The only alternative for investigating the incommensurate phase is solution of the $(3+n)$-dimensional crystal structure through the intensities of the satellite Bragg reflections.

This study confirms previous electron-diffraction results of Withers *et al.* that the alkaline-earth orthosilicates represents another series of β-K_2SO_4-type A_2BX_4 inorganic compounds which undergo the $\beta \rightleftarrows \alpha$ transition with an intervening incommensurate phase. For Sr_2SiO_4, the modulation wave appears to be pinned up to 200 °C and the temperature dependence of the soliton density near T_c is similar to that of Rb_2ZnCl_4, having a nonzero n_s below T_c on cooling but not on heating through the transition.

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