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Neutron scattering study of the soft optic mode in $SrTiO_3$ under a high magnetic field

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According to the vibronic theory of ferroelectric phase transitions, appreciable shifts in T_c, with corresponding shifts in soft-mode frequencies, should be observable under high-magnetic-field conditions. The field effects have been predicted to be much larger in wide-gap than in narrow-gap materials. Neutron scattering measurements on the soft optic zone-center mode in $SrTiO_3$ were carried out under magnetic fields up to 70 kOe over a temperature range of 4.5 to 50 K. No magnetic-field-induced shifts of the soft-mode frequency were observed.

I. INTRODUCTION

Over the past decade, the soft-mode concept, as developed by Cochran, Anderson, and Ginzberg,[1–3] has become established as a benchmark for most studies of ferroelectric transitions, and indeed of structural phase transitions in general. The essential validity of this lattice dynamical theory has been demonstrated in numerous experimental studies.[4] In recent years, with what has become known as the "vibronic theory,"[5–7] an attempt has been made to provide a microscopic explanation of the ferroelectric soft mode instability on the basis of the interband electron-phonon interaction. In this pseudo-Jahn-Teller description, the basic statement is that under certain conditions temperature-dependent mixing of the ground electronic state with nearby excited states by the dynamical dipolar nuclear displacements results in a softening or instability of the high-symmetry structural configuration with regard to these displacements.

In some of the more recent investigations,[8–10] relatively large magnetic field effects on the transition temperature (or the soft-mode frequency) have been predicted on the basis of the vibronic theory, and this field dependence would therefore seem to offer a definitive means for experimental testing of the theory. An observed shift in T_c due to a magnetic field in the narrow gap ferroelectric $Pb_{1-x}Ge_xTe$ has already given some support to the theory.[11] Somewhat surprisingly, the magnetic field effect on wide gap ferroelectrics has been predicted by Vekhter *et al.*[9] to be even larger than on narrow gap ferroelectrics. In particular, calculations by these authors indicate that a magnetic field of 100 kOe should cause a 5 to 10% change in the Curie temperature in the case of "doped" $SrTiO_3$. The dopant and its concentration were not specified; however, the lattice dynamical data used in the calculation were those reported by Cowley for a nominally pure sample.[12]

Actually, some doped samples of $SrTiO_3$ are well known to have magnetic *field-independent* capacitances at low temperatures, and indeed have even been used as temperature sensors for experiments under high magnetic field conditions.[13] However, it is not so clear that the field-independent properties of these materials constitute immediate experimental evidence against the predictions based on vibronic theory. $SrTiO_3$ has been doped in many different ways, with widely differing effects on its physical properties.

In any event, since no population of the conduction band is required in the treatment by Vekhter *et al.*, their calculations would appear to be applicable to the pure dielectric material. The purpose of the present communication is to report inelastic neutron scattering measurements on the soft optic zone center ferroelectric mode of a nominally pure sample of $SrTiO_3$ under magnetic fields up to 70 kOe. Within the limit of our experimental detectability, no magnetic field-induced shifts of the soft-mode frequency could be observed.

II. EXPERIMENTAL

The neutron scattering experiments were performed on a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor with a $SrTiO_3$ single crystal obtained from the National Lead Corp. with a volume of about 2 cm^3. Pyrolytic graphite monochromator and analyzer crystals were used in conjunction with a pyrolytic graphite filter to suppress higher-order neutron wavelengths. Preliminary measurements showed that the optimal experimental conditions for energy resolution consisted of using the usual (002) reflection of the monochromator but the

(004) reflection of the analyzer, with collimations of $20' \times 20' \times 20'$ (in pile, monochromator-to-sample, sample-to-analyzer) and $40'$ for the analyzer-to-detector collimation.

The incident neutron wave vector was 2.67 Å^{-1} and the scattering measurements were carried out in the (*hhl*) reciprocal plane, mostly around the (002) zone center. In order to avoid background effects due to the large (002) Bragg peak in $SrTiO_3$, the data used for field-on and field-off comparisons were collected at small reduced wave vectors of (0.01, 0.01, 0) or (0.015, 0.015, 0) instead of exactly at zone center.

A vertical magnetic field up to 70 kOe was provided by a superconducting magnet. Temperature was measured by a magnetic field independent carbon-glass resistance thermometer. The temperature was regulated well within 0.1 K.

III. RESULTS AND DISCUSSION

Although $SrTiO_3$ is only an incipient ferroelectric, and does not undergo a phase transition with the development of a spontaneous polarization, the square of the soft-mode frequency, ω^2, varies linearly with $T - T_c$ over a considerable range (where T_c can be regarded as the apparent ferroelectric transition temperature of the material). Taking as a reference the Curie-Weiss relation fitted to the detailed experimental data of Yamada and Shirane,[14] one obtains a "T_c" of 38 K (which is close to the value of 30 K assumed by Vekhter *et al.*[9]). Hence, the 5 to 10% effect predicted by Vekhter *et al.* at a field of 100 kOe corresponds to a shift in T_c of 2 to 4 K. Since the maximum field available for this study was only 70 kOe and the theoretical shifts vary with the square of the field, the predicted ΔT_c range appropriate to our experiment is 1 to 2 K.

As a preliminary step, experimental sensitivity was tested in a simulation of a 2 K shift by measurements of the soft-mode frequency at temperatures of 48 and 50 K, within the range of linear variation of ω^2 with $T - T_c$. The well-separated cross sections obtained at these temperatures are shown in Fig. 1. (The difference in phonon intensities is to be expected from the proportionality of intensity to $1/\omega^2$.) From these measurements, we visually estimate an experimental sensitivity of better than 0.08 meV (about 30% of the energy shift of $\Delta\hbar w = 0.26$ meV). Since this was more than adequate for our experimental objectives, no attempt was made to pin down sensitivity more precisely by error analysis of fitted profiles. This sensitivity can be viewed in terms of an equivalent shift in T_c by making use of the quadratic relationship between $\hbar\omega$ and T_c. At $T \sim 50$ K, a shift in T_c of 1 K (the lower limit of the theoretically expected shift) corresponds to an energy shift of ~ 0.15 meV, which is about twice as large as the experimental sensitivity.

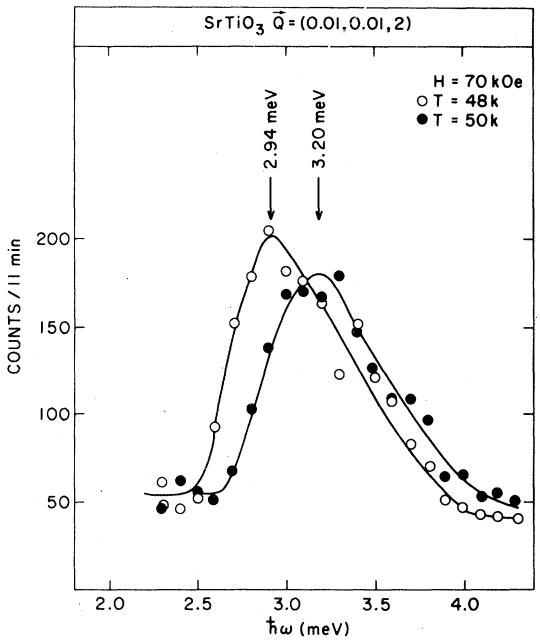

FIG. 1. Comparison of the ferroelectric soft-mode cross sections of $SrTiO_3$ at 50 and 48 K. Both measurements were taken under a magnetic field of 70 kOe, and at the reduced wave vector (0.01, 0.01, 0) in the (002) zone.

(The expected energy shifts become even larger as T_c is approached.)

Measurements performed at 4.5, 20, 30, 35, 39, and 50 K with and without a magnetic field of 70 kOe failed to reveal any measurable field-induced soft-mode frequency change. Figures 2(a) and 3(a) show typical measured cross sections obtained at the two extreme temperatures of 50 K (above "T_c") and 4.5 K (below "T_c") for reduced wave vectors $\vec{q}$ of (0.01, 0.01, 0) and (0.015, 0.015, 0), respectively.

The broadening of the phonon line profiles is mostly due to the instrumental vertical resolution in the presence of a sharp phonon anomaly with a rapidly varying dispersion surface. The resolution corrected cross sections shown in Figs. 2(b) and 3(b) show that the broadening observed on the raw data when going from 50 to 4.5 K is due to the sharpening of the soft phonon dispersion branch with decreasing temperature. The intrinsic phonon line width after resolution correction, even shows a narrowing at 4.5 K, in agreement with the earlier observations by Yamada and Shirane.[14]

In conclusion, we do not observe any magnetic field effect on the soft-mode behavior in $SrTiO_3$. Some possible questions on this problem were not explored, however. One could be the possibility of anisotropy in a field effect. Isotropic parabolic bands were assumed in the calculations of Vekhter *et al.*,

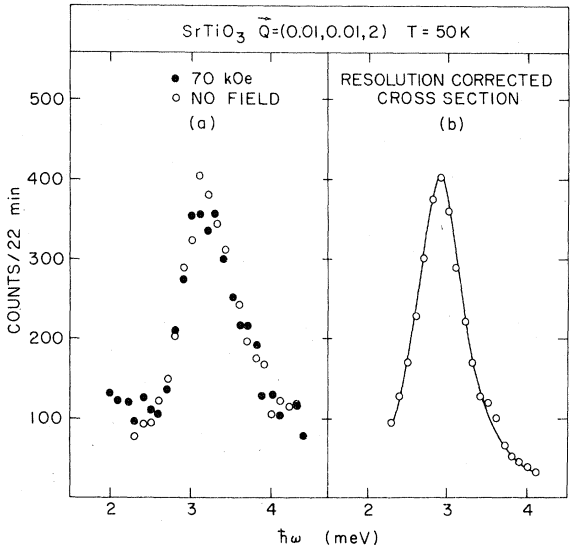

FIG. 2. (a) Typical cross sections of the ferroelectric soft mode of $SrTiO_3$ under a magnetic field of 70 kOe (full circles) and without field (open circles). Measurements were taken at 50 K, at the reduced wave vector (0.01, 0.01, 0) in the (002) zone. No detectable field-induced frequency shift is observed. (b) Resolution corrected cross section, taking into account the instrumental horizontal and vertical resolution and the soft phonon branch dispersion at 50 K. The dispersion at the zone center was approximated by an isotropic relation of the form $\omega = a + bq^2$.

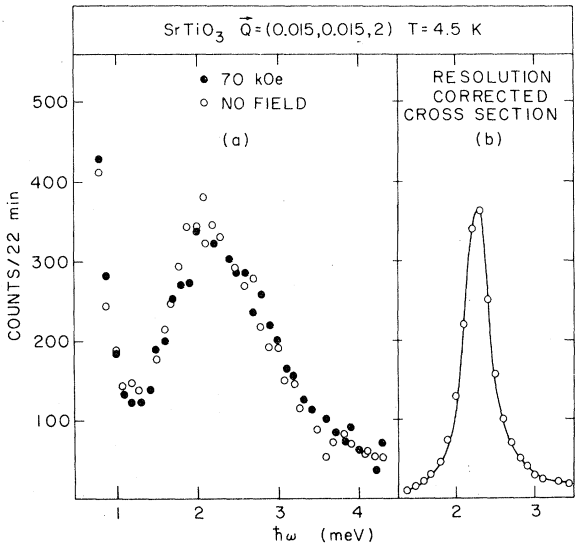

FIG. 3. (a) Typical cross sections of the ferroelectric soft mode of $SrTiO_3$ under a magnetic field of 70 kOe (full circles) and without field (open circles). Measurements taken at 4.5 K at the reduced wave vector (0.015, 0.015, 0) in the (002) zone. No detectable field-induced frequency shift is observed. The broadening of the scans in Fig. 3 compared to those in Fig. 2 is due to the instrumental vertical resolution in the presence of a sharpened dispersion surface. (b) Resolution corrected cross section, taking into account instrumental horizontal and vertical resolutions, and the soft phonon branch dispersion at 4.5 K.

and in our experiment, the magnetic field was parallel to a [110] direction in the crystal and perpendicular to the scattering plane (i.e., to the scattering and wave vectors). The present results could be inconclusive if more detailed calculations were to indicate strong directional dependence for the field effect.

Another question concerns the possibility that a field effect could depend on suitable doping. As noted earlier, the specially doped $SrTiO_3$ temperature sensor materials exhibit field independence in their dielectric properties.[13] However, the ferroelectric soft-mode behavior of $SrTiO_3$ is known to be highly sensitive to oxygen vacancy and "free" electron concentrations.[15] It is conceivable that a field effect could require favorable placement of particular impurity levels.

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