Central-Peak Enhancement in Hydrogen-Reduced $SrTiO_3$

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A neutron-scattering study of the structural phase transition in hydrogen-reduced crystals of $SrTiO_3$ shows a systematic enhancement of the central-peak intensity with increasing defect concentration. T_c is found to decrease linearly with increasing carrier concentration. The results provide direct experimental evidence for the involvement of a defect mechanism in central-peak formation.

In this Letter we report neutron-scattering measurements which demonstrate for the first time a systematic central-peak enhancement with defect concentration for a structural phase transition. Using hydrogen-reduced samples of $SrTiO_3$, prepared and characterized in an earlier study of the superconducting properties,[1] the central-peak intensity was found to increase steadily with defect concentration. In addition, the transition temperature (~ 105 K in normal unreduced material) was found to decrease linearly with increasing carrier concentration (the only measure presently available of defect concentration).

Since the discovery[2] of the central peak in $SrTiO_3$ its characteristics have been extensively investigated.[3,4] Its intensity diverges as T_c is approached from above, while the frequency of the soft phonon at the R point decreases to a small (but finite) value at T_c. The energy width of the peak is so narrow that no spectroscopic experiment to date has been able to establish any more than an upper limit on the linewidth[5] above T_c (see, however, a recent report by Lyons and Fleury of an anomalous central peak of measurable width just below T_c in $SrTiO_3$).[6] This latter property has posed a particular difficulty for the development of intrinsic dynamical models for the central peak, and has led several authors to consider lattice defect or impurity mechanisms as possible explanations for its occurrence.[4,7-9] In particular, Halperin and Varma[4] have developed a detailed microscopic theory of defect mechanisms which yields a narrow central component. Until now, however, there has been little direct experimental evidence to support a role for defects in central-peak formation.[10]

Neutron-scattering data were collected at the Brookhaven National Laboratory high-flux beam reactor on a triple-axis spectrometer. A pyrolytic graphite monochromator, analyzer, and double filter to eliminate harmonics, were used with an incident neutron energy of 13.5 meV. The hydrogen-reduced samples of $SrTiO_3$ were single crystals with volumes of a few tenths of a cubic centimeter.

The sample carrier concentrations, used here for relative measure of the presence of defects, were determined previously from Hall-effect measurements.[1] Although it has been demonstrated that the defect concentration in hydrogen-reduced $SrTiO_3$ is closely comparable to and increases with the carrier concentration,[11] insufficient data exist to establish a functional relationship over the concentration range of the present study. One of the defects present in the hydrogen-reduced material has been identified by electron-spin resonance as a Ti^{+3} ion at the Sr^{+2} site, but displaced towards one of the near-neighbor oxygens.[12,13] This particular defect couples linearly to the order parameter for the structrual phase transition.

The T_c for each sample was determined by monitoring the intensity of a strong Bragg peak, $Q=(1,1,1)$. On cooling through T_c there is a relief of extinction, due to the formation of domains, with an attendant marked increase in the Bragg intensity. These measurements were in accord with earlier[14] ultrasonic observations of lowered T_c's in hydrogen-reduced material. In addition, however, it was found that T_c decreases linearly with increasing carrier concentration, at least over the range of n_c covered in these experiments. This is shown in Fig. 1. A decrease in T_c with increasing defect concentration is predicted by Halperin and Varma[4] for their "frozen"-defect case, in contrast to a predicted increase in T_c for relaxing defects. Central-peak development is predicted for both cases.

The behavior of the central peak with increasing carrier concentration was determined by measuring the integrated intensity of the central component above T_c as a function of temperature. In all cases the values of $T - T_c$ were chosen so that the phonon side bands were well separated from the central component. This was confirmed in constant-Q scans at the R point. Figure 2

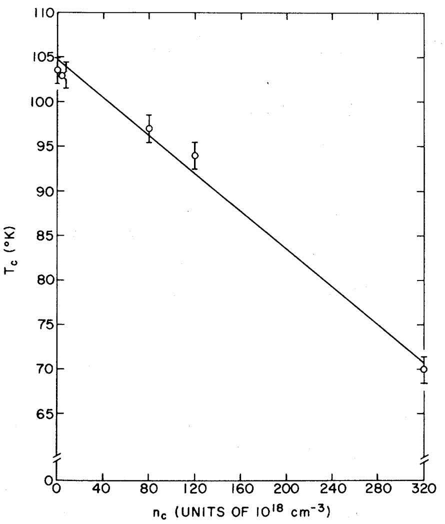

FIG. 1. Variation of T_c with carrier concentration in hydrogen-reduced $SrTiO_3$. Solid line is a linear fit to the data.

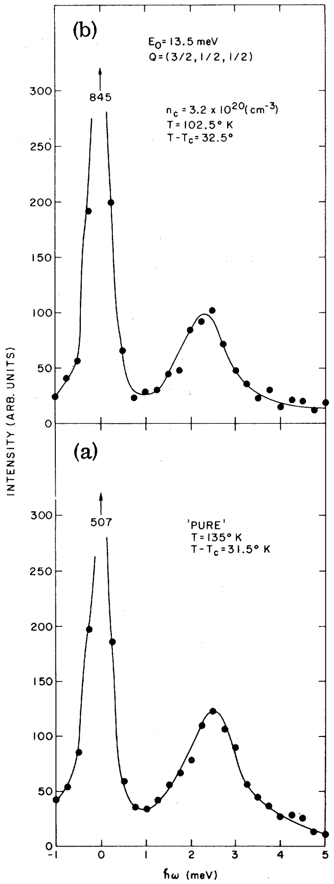

FIG. 2. Typical constant-Q scans at the R point (a) for a "pure" reference sample of $SrTiO_3$ and (b) for the hydrogen-reduced sample with highest carrier concentration.

shows scans for the "pure" and most heavily doped samples. These scans show no broadening of the soft phonons, within measurement statistics and spectrometer resolution, even for the highest carrier concentration. Also, the variation of the soft-mode frequency as a function of $T - T_c$ was nearly the same for all samples. Since any energy width of the central peak is much narrower than our instrumental resolution, scans for $E = 0$ are in fact an integral in energy over the central peak. Constant $E = 0$ scans were performed and the intensity integrated over Q in order to remove any effects from different mosaic spreads in each sample. The corrections for variations in sample volume were taken care of by comparing the integrated intensities of an acoustic phonon along with check comparisons of the incoherent scattering at fixed Q. The contribution of the incoherent scattering from the Ti atoms at Sr sites even for the most concentrated sample is small compared to the incoherent scattering from the Ti sublattice.

In Fig. 3 we plot the integrated central-peak intensities versus the temperature difference $T - T_c$ for the various samples studied. The "pure" sample is an unreduced reference sample cut from one of the some boules used in the hydrogen-reduction preparations.[1] It is apparent from these curves and the central peak in Fig. 2 that the intensity is enhanced by increases in the carrier concentration n_c and thereby with increases in n_d, the concentration of Ti^{+3} defect centers.

In a sufficiently dilute system of randomly distributed defects, the intensity should be simply proportional to the defect concentration. Comparison of the curves in Fig. 3, however, shows that intensity observed for the most heavily reduced sample is only a few times higher than that of the least reduced (at the same value of $T - T_c$), even though n_c is up by over two orders of magnitude. The limited data available from Phillips *et al.*[11] indicate that between two and four carriers are produced for every Ti^{+3} center, in a concentration range roughly comparable to that of the present study. Assuming for crude estimate purposes that $n_c \simeq 3n_d$, then n_d for our samples would range from about 6×10^{17} to about 1×10^{20} Ti^{+3} centers per cubic centimeter. This is equivalent to a range of average defect spacings of about $5\frac{1}{2}$ to 30 unit cells, or about 22 to 120 Å. Since the correlation length at T_c in pure $SrTiO_3$

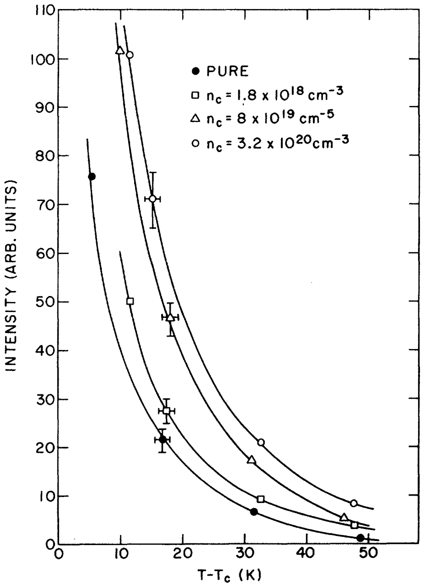

FIG. 3. Integrated central-peak intensity of hydrogen-reduced $SrTiO_3$ as a function of $T - T_c$. Data for $n_c = 1.20 \times 10^{20}$ cm^{-3} are omitted for clarity in the presentation since they are nearly the same as for $n_c = 8 \times 10^{19}$ cm^{-3}. Typical error limits are shown. The solid lines are guides for the eye.

has been estimated[4] at about 30 Å, it is not surprising that the intensities observed in the present experiment are related to n_c in a highly nonlinear manner. Only one of the sample ($n_c = 1.8 \times 10^{18}$) would appear to be sufficiently dilute for linearity to hold. If the latter is the case, incidentally, our intensity data, and the assumption made above relating n_c and n_d, would imply a defect concentration for the "pure" reference sample of about 4×10^{17}/cm^3, or about 2.5×10^{-5} for the ratio of defect to normal cells. This is not an unreasonable number.[4]

Phenomenological models imply that no single power law can describe the divergent behavior of the central peak over the entire temperature range. Far from T_c the divergence should go as $(T - T_c)^{-2}$, but near T_c is should diverge linearly with $(T - T_c)^{-1}$. Our data are consistent with this type of behavior.

In summary, we have shown directly that defects can enhance the central peak in a structural phase transition. The particular defects studied appear to be of the frozen-defect type discussed by Halperin and Varma.[4] The results do not demonstrate that the central peak originates solely from defect mechanisms. Since it is well known, however, that all "pure" materials crystallize with some concentration of defects, the results indicate that their contributions must be considered seriously in assessing intrinsic dynamical mechanisms. Further experiments are planned at lower defect concentrations with more fully characterized samples so that the defect mechanism can be examined on a more quantitative basis.

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