APPENDIX A

Dynamical light scattering study in a chiral smectic C liquid crystal

A.1 Introduction

Continuing our work on the optical diffraction in the Sc* liquid crystalline phase of SCE6, we have also studied this compound using dynamic light scattering. As described earlier Sc* liquid crystal has a helical structure constituted of layers of tilted molecules. The director, that is, the average tilt of the molecules in the layer, makes a constant angle with the layer normal and rotates uniformly from one layer to another. This tilt and the azimuth of the director are considered as the order parameters in the Sc* phase for the Smectic A - Sc* phase transition. The thermal fluctuations of these order parameters give rise to strong scattering of light. Dynamic light scattering is a powerful technique to study the order parameter fluctuations at the Smectic A - Sc* transition and in the Sc* phase [1,2,3,4] wherein one looks at the temporal variation of the scattered light from the sample. The thermal fluctuations of the molecular tilt angle is known as the soft mode, and the fluctuation of the azimuth of the tilt is called the Goldstone mode [1,5] of the smectic A - Sc* transition. The soft mode which represents the fluctuations in the molecular tilt, involves change in layer spacing and hence cost more energy to get thermally excited in the Sc* phase. It can only be observed near the Smectic A - Sc* transition temperature. Far away from the transition the soft mode is suppressed by the Goldstone mode. It is possible to observe the soft mode inside the Sc* phase

in the presence of a biased electric field.

In the optical spectrum one can get these modes in the vicinity of the direct beam in the Bragg mode and in the vicinity of any diffraction order in the phase grating mode. At a given temperature the measurement of relaxation frequency of the Goldstone mode also allows us to calculate the ratio of elastic constant to viscosity coefficient which is a very useful parameter in the application of ferroelectric liquid crystals in optical devices like light modulators [6] and display devices [7].

A.2 Description of the Experiment

Studies were carried out in cells with sample alignment in both Bragg and phase grating modes. For the alignment in the Bragg mode, cleaned glass plates are coated with ODSE (0.1% Octadecyl triethoxy silane in tolune solvent) and cured at 150°C. Cells were made using **23** μm mylar spacers. For the Bragg geometry, the cell was filled with the sample in the isotropic phase and cooled slowly to the Sc* phase. The alignment was checked with the polarizing microscope. At the cholesteric - Srnectic A transition the uniform black appearance of the sample indicated a good alignment in the Bragg geometry. On cooling further the Sc* phase appears with a uniform grey texture. For the cells with alignment in the phase grating mode, procedure described in chapter **4** was applied. Mylar spacer of 50μm was used for preparing cells in the phase grating geometry.

After the alignment the sample was transferred to a hot stage Mettler (FP82). The temperature of the sample is controlled with a resolution of $\pm$0.1 °C. A I-Ie-Ne 35 mwatt laser light with polarization parallel to the scattering plane is incident on

the sample. The scattered light is analyzed in the polarization orthogonal to the scattering plane. A Malvern (4700c) 128 channel correlator was used to acquire the intensity autocorrelation data. For the Goldstone mode the sample time was of the order of few microseconds. A typical intensity autocorrelation data obtained for SCE6 in the Sc* phase is shown in figure A.1. This data was fitted to a exponential function given by

$$G_2(t) = a + b\ exp(-t/\tau) \tag{1}$$

where a is the background noise, b depends on the experimental conditions and τ is the relaxation time. Experiment was performed at various scattering angles for different temperatures. The whole setup was checked with a previously studied sample CE8 [2]. The measured relaxation time for CE8 was in good agreement with the earlier measured values.

A.3 Theory

Following a simple Landau theory of phase transitions one can write the relaxation frequency of the Goldstone mode for the Sc* [1,2] as

$$\frac{1}{\tau_G} = \frac{K_2}{\gamma}(q_z - q_o)^2 + \frac{K_+}{\gamma}q_x^2 \tag{2}$$

where q_o is the wave vector of the helical structure of the Sc* phase and related to the pitch P of the sample by the relation $q_o = 2\pi/P$, q_z and q_x are the scattering wavevector components along Z and X direction respectively, γ is the viscosity coefficient. K_+ is related to splay and bend elastic constants K_1 and K_3 respectively by the relation $K_+ = (K_1 + K_3)/2$, and K_2 is the twist elastic constant. Here Z is

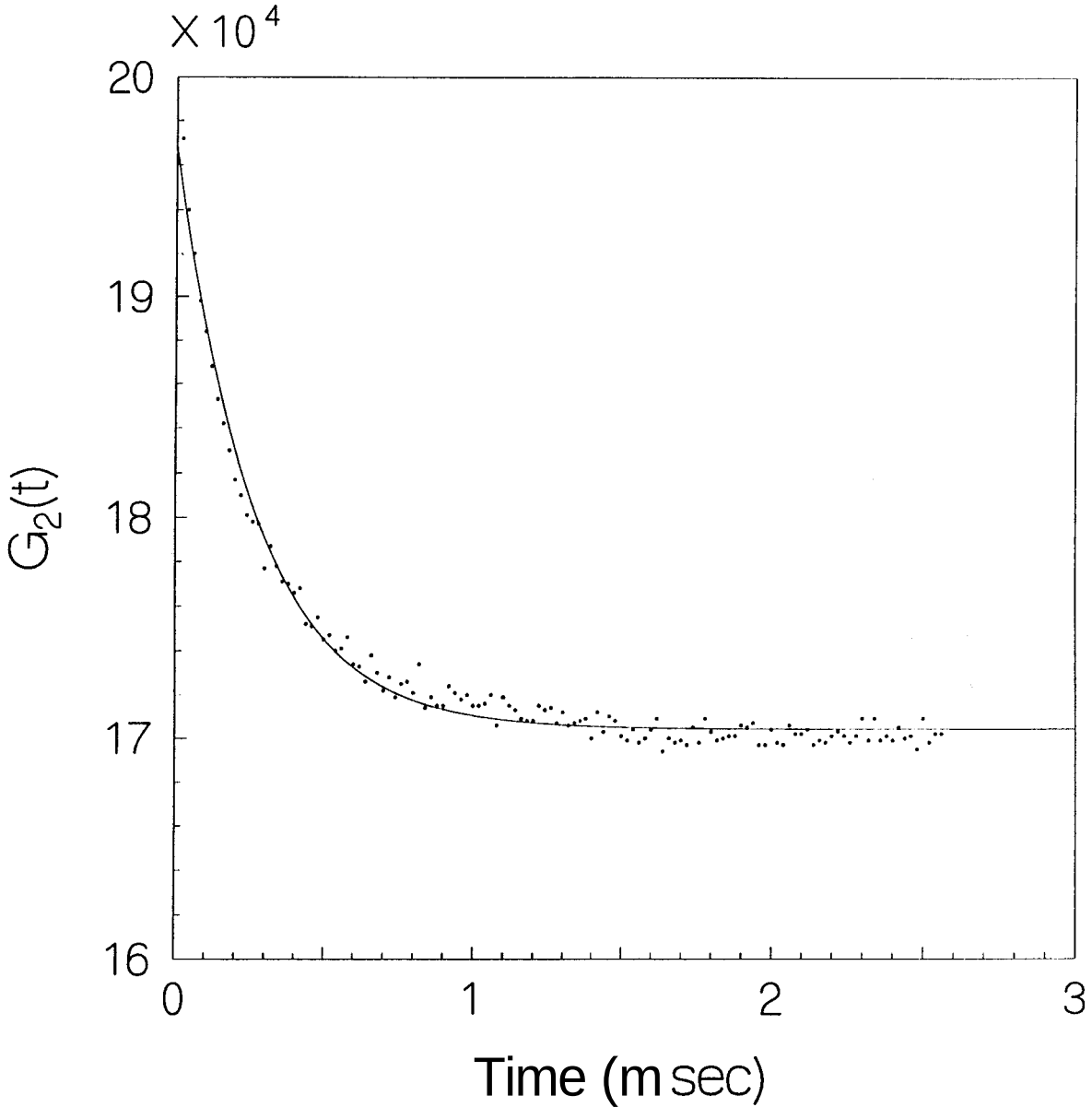

Figure **A.1:** A typical scattered Intensity autocorrelation data obtained in the Sc* of SCE6 sample 5.0°C below T_c . The data was fitted to a single exponential. Scattering angle = 12°.

to be taken as the twist axis. For the Bragg geometry (See figure A.2) we can write

$$q_z = \mid q \mid Sin(\theta_s/2) \quad and \quad q_x = \mid q \mid Cos(\theta_s/2) \tag{3}$$

where $\mid q \mid = 2kSin(\theta_s/2)$, k $= 2\pi/\lambda$ being the incident wavevector. At a given temperature the relaxation frequency data for different scattering angles was fitted to equation 2 and ratios K_+/γ and K_3/γ were obtained.

A.4 Results and Discussion

The temperature dependence of the Goldstone mode across the transition at the fixed scattering angle is shown in figure A.3. These measurements were done with sample alignment in the phase grating mode. The appearance of the diffraction pattern as we cool the sample from the Smectic A phase indicates the transition to the Sc* phase. We notice that the relaxation frequency of the Goldstone mode falls sharply at the Smectic A - Sc* transition but in the Sc* phase there is not much variation in it.

Scattering angle dependence of the Goldstone mode at a given temperature for SCE6 is given in figure A.4. These measurements were done with sample aligned in the Bragg geometry. As expected by the simple Landau theory the inverse of relaxation time is dependent quadratically on the scattering angle. The data points were fitted to equation 3 to obtain the values of K_+/γ and K_2/γ for different temperatures. The resulting values of K_+/γ and K_2/γ for the SCE6 are listed in following Table.

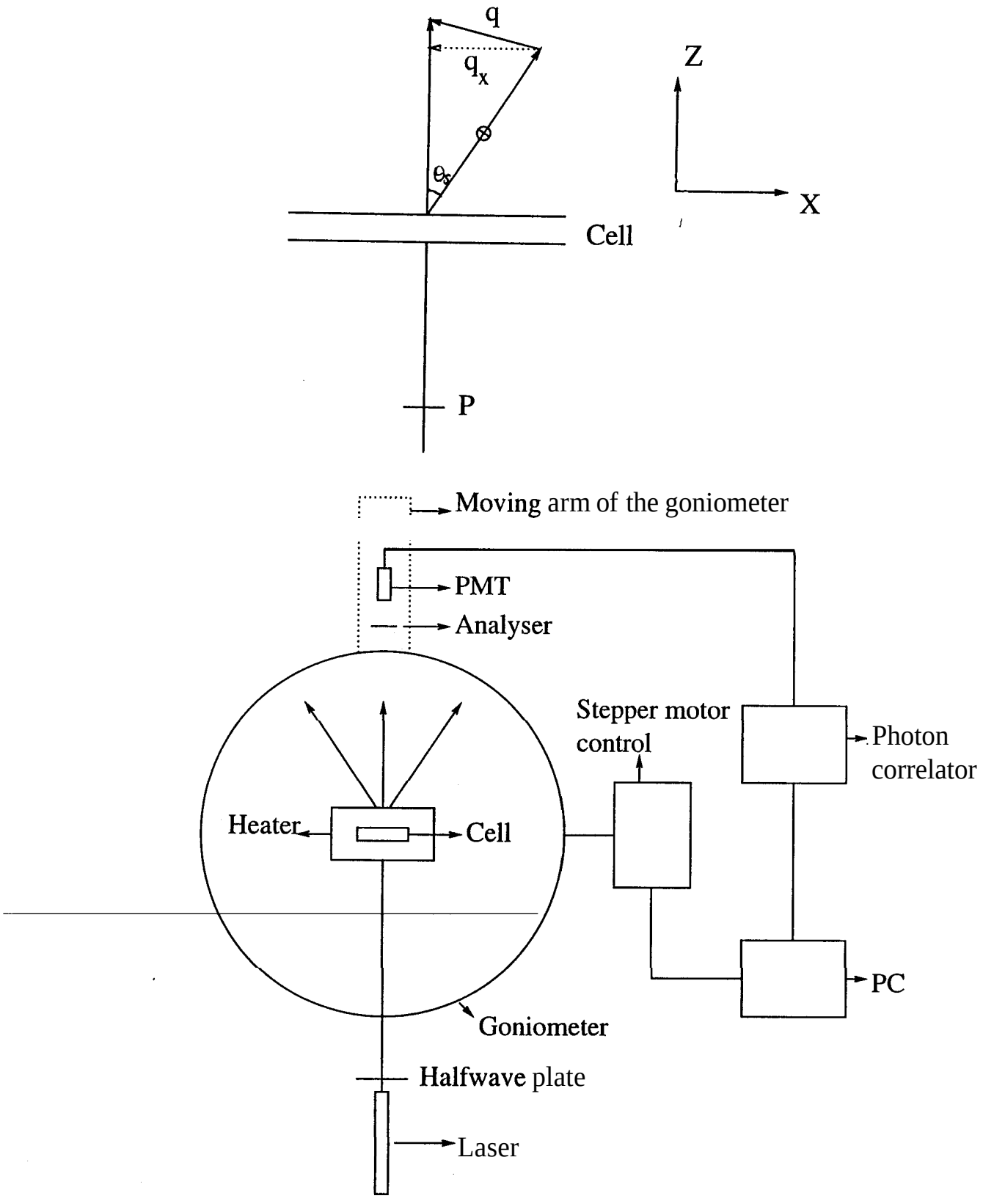

Figure **A.2:** Schematic diagram of light scattering geometry and the setup used for dynamic light scattering experiment.

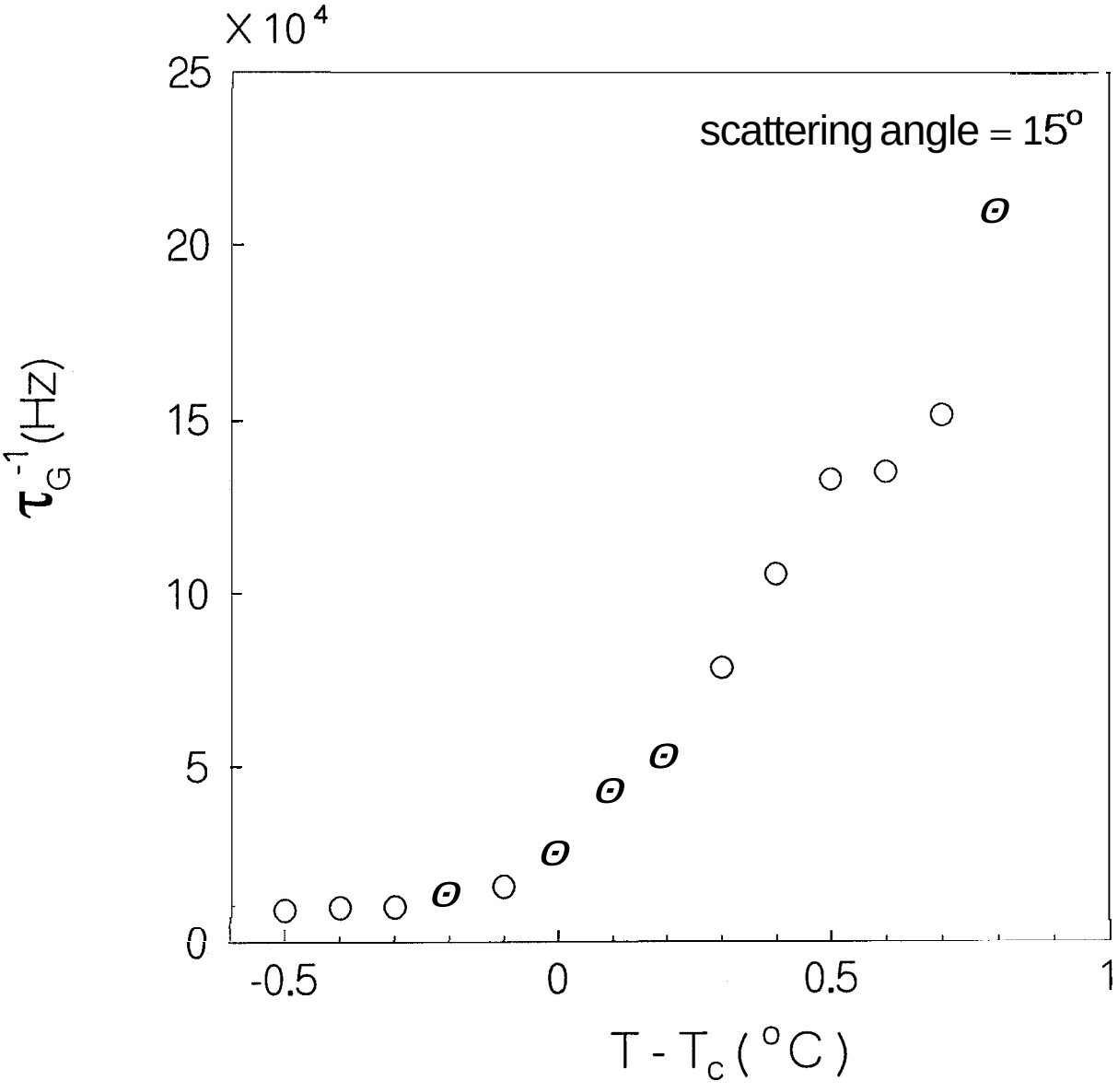

Figure **A.3:** The measurement of the relaxation frequency of the Goldstone mode across the Smectic **A** to Sc* phase transition. The data was taken for a sample aligned in the phase grating mode. scattering angle = 15°.

$T - T_c(°c)$	$K_2/\gamma(cm^2s^{-1})$	$K_+/\gamma(cm^2s^{-1})$
-0.3	$1.08\pm0.135 \times 10^{-6}$	$2.82\pm0.350 \times 10^{-7}$
-1.3	$4.05\pm0.848 \times 10^{-6}$	$5.08\pm0.722 \times 10^{-7}$
-2.3	$6.36\pm0.529 \times 10^{-6}$	$7.33\pm0.609 \times 10^{-7}$
-3.3	$7.79\pm0.569 \times 10^{-6}$	$8.98\pm0.655 \times 10^{-7}$
-4.3	$8.43\pm0.960 \times 10^{-6}$	$9.72\pm0.110 \times 10^{-7}$
-5.0	$7.26\pm0.619 \times 10^{-6}$	$8.50\pm0.724 \times 10^{-7}$
-9.3	$7.24\pm0.693 \times 10^{-6}$	$9.16\pm0.876 \times 10^{-7}$

These values are in agreement with those reported in the literature for similar materials by the light scattering studies [2,8,9,10].

In this compound, in addition to the relaxation of the Goldstone mode in the Sc* phase we can also observe a relatively slow relaxation for the samples aligned in the phase grating mode. To show this slow relaxation, we have taken the intensity autocorrelation for sample time of few milli seconds. A typical autocorrelation curve is shown in Figure **A.5.** We find that the relaxation frequency of this mode is few Hertz and is almost independent of the scattering angle. It is worth mentioning here that dielectric studies is some of Sc* compounds indeed show this kind of new relaxation modes apart from Goldstone and the soft modes [11].

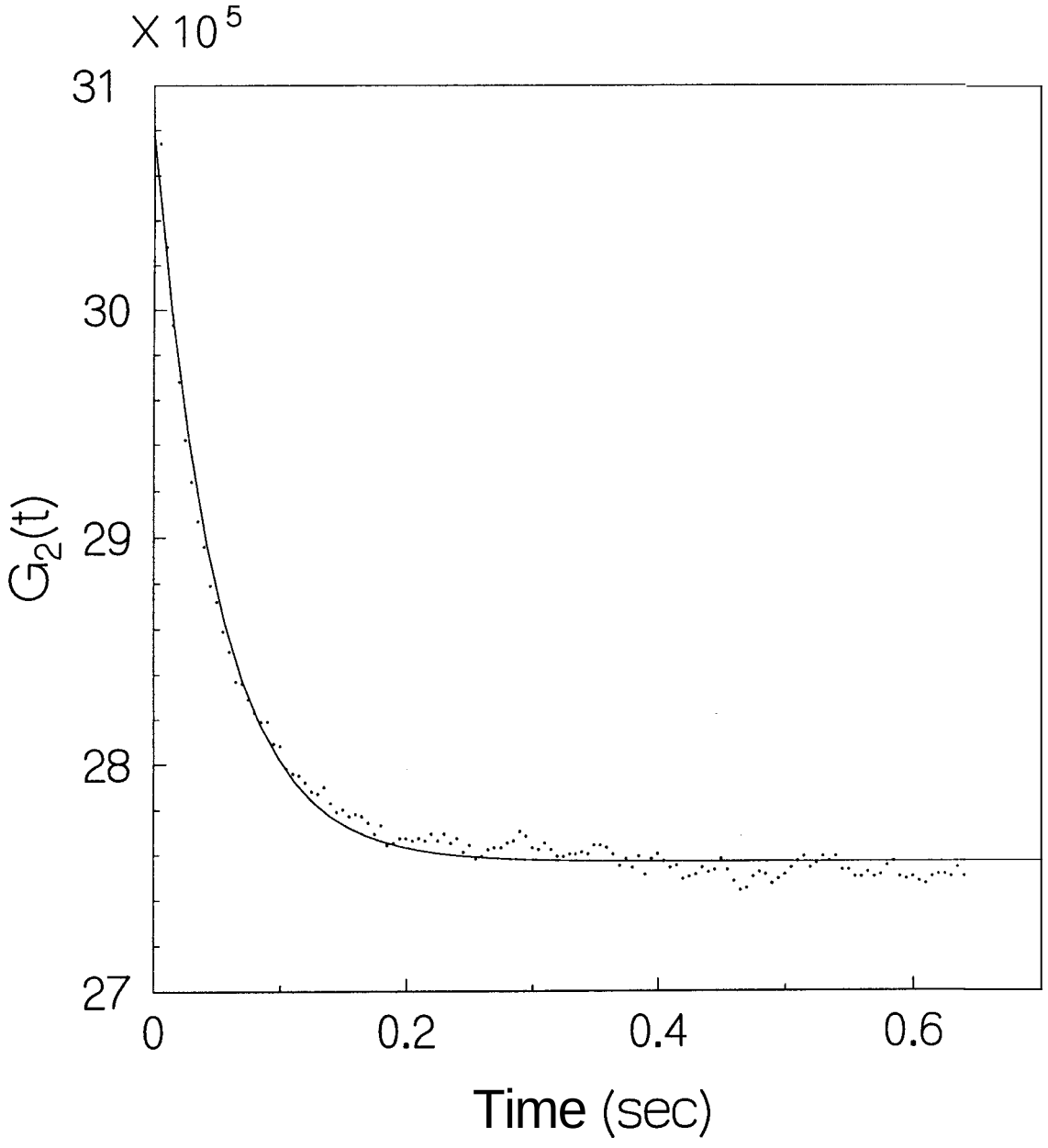

Figure **A.5:** The observed slow relaxation in the Sc* phase of SCE6 sample aligned in the phase grating mode 0.2°C below T_C. Scattering angle = 19°.

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APPENDIX B

Optical diffraction in some Fibonacci structures

During our studies on quasi-periodic cholesteric medium, we also got interested in optical diffraction in some other types of quasi-periodic phase and amplitude gratings. In the case of phase grating we consider a grating with quasi-periodic step heights. In the case of amplitude gratings we have looked into the optical analogues of quasi-periodic crystals with a Fibonacci sequence in the atomic form factor and interatomic distances. Possibilities of such structures which are accessible in the X-ray region have not been looked into so far.

B.1 Step phase gratings

Periodic phase gratings involving optical steps are well known [1]. Here we consider periodic gratings but with the optical steps of heights H_1 and H_2 arranged according to the FS : $H_1, H_2, H_1, H_1, H_2, H_1, H_2 ...$ For an incident plane wavefront both the steps H_1 and H_2 have the same width but different optical paths. We assume H_1 to have a longer optical path length compared to H_2. We use the RN theory to work out the diffraction pattern. In our computations we assume the sample to be uniformly $20\mu m$ thick, but the refractive indices for the steps H_1 and H_2 are 1.58 and 1.5 respectively and each step has width of $5\mu m$. The diffraction pattern is found not to be dependent on grating width when the grating has 400 or more elements. This is depicted in figure B.1. The diffraction pattern is symmetric. All

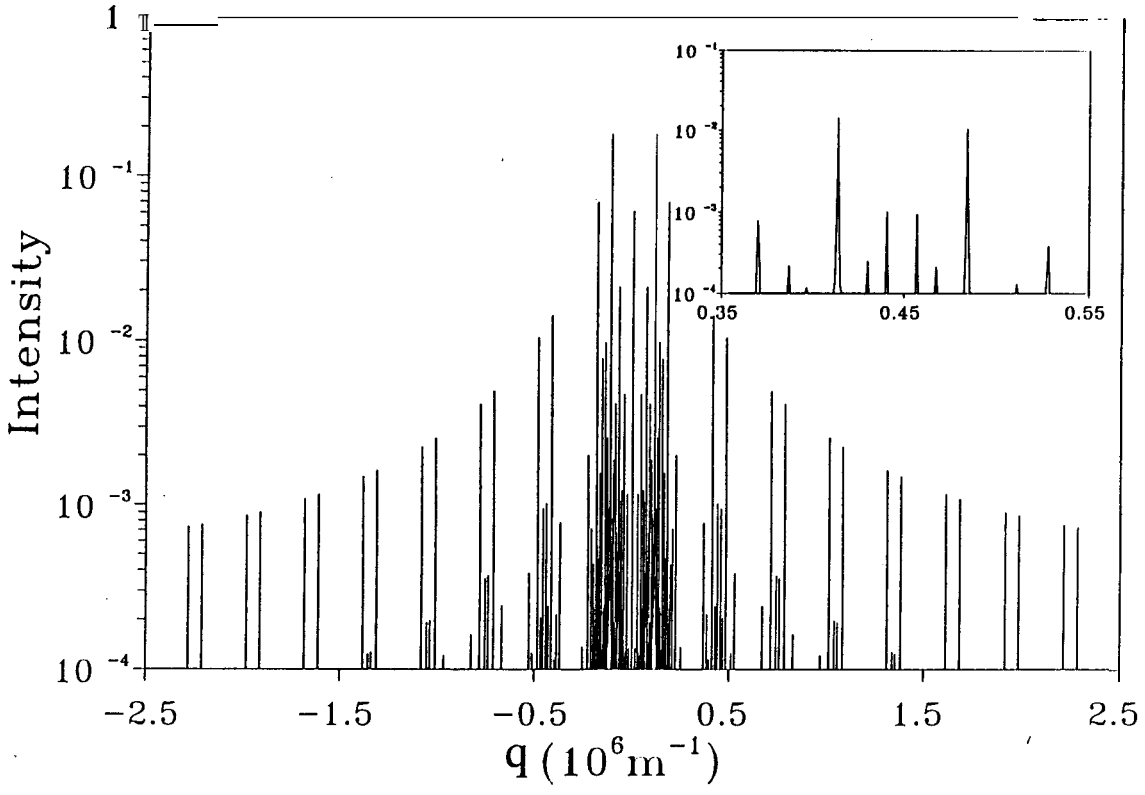

Figure B.1: Diffraction pattern of a step phase grating with step height H_1 and H_2 arranged in a Fibonacci sequence.

the diffraction orders have same diffraction features. It must be remarked that in the case of normal periodic step gratings with the same number of elements one gets sharp peaks. But in the present structure each diffraction order has a small spread. This spread is due to the fact that each diffraction order has a fine structure (see inset figure B.1). This fine structure is same in all the orders and is independent of lattice size and persists even when we take many more diffracting elements.

B.2 Amplitude gratings

Optical diffractions in quasi-periodic amplitude gratings have been studied both experimentally and theoretically by Tanibayashi [2]. He found that the diffraction pattern has not only a rich structure but is also self-similar. We consider here two different types of quasi-periodic amplitude gratings not so far considered by others.

The first type of grating is a sequence made up of two slits of widths S_1 and S_2 (which are incommensurate) occurring according to the usual FS, but on a periodic lattice with an edge to edge separation of D, i.e., the sequence of the elements is : $S_1, \mathrm{D}, S_2, \mathrm{D}, S_1, \mathrm{D}, S_1, \mathrm{D}, S_2, \ldots$. This structure is rather analogous to a one-dimensional periodic crystal with FS in atomic form factors.

In the second type of grating, the slit width S as well as the edge to edge separation D between neighbouring slits occur in a FS i.e., the sequence is : $S_1, D_1, S_2, D_2, S_1, D_1, S_1, D_1, S_2, \ldots$. Also the two slit widths S_1 and S_2, as well as the slit separations D_1 and D_2 are considered to be incommensurate. This is analogous to a one dimensional quasi-periodic crystal in which atomic form factors and the interatomic distances occur according to a FS.

We have calculated the diffraction pattern for first **400** continuous elements of M_{14} sequence. In figure B.2a we have given the computed pattern obtained in the first type of grating. Here the intensity of different orders is plotted as a function of the scattering wavevector q which given in equation (6.7). Unlike in the periodic gratings here the diffraction peak position is dependent on a pair of integers. The second type of grating results in a diffraction pattern shown in figure B.2b.

We have also investigated both these cases when either S_1 or S_2 is absorbing i.e. it is masked with a material with complex refractive index. With S_2 absorbing, the diffraction pattern has been computed. We find not only some extra orders, but also an asymmetric diffraction pattern. This is shown in figures B.3a and B.3b. We can understand asymmetry in the pattern by appealing to the symmetry of the lattice. For example a periodic lattice with a pair of slits at each lattice point is in general non-centrosymmetric and with one of the slits absorbing the diffraction pattern is always asymmetric. This is due to the fact that the absorbing element contributes an extra phase. This results in an asymmetry in the diffraction pattern. This is the optical analog of an equivalent result in X-ray diffraction from absorbing non-centrosymmetric crystals [3]. It is now well established **[4]** that Fibonacci sequence is a non-centrosymmetric in nature. Hence if it has absorbing elements, it will result in an asymmetric diffraction pattern.

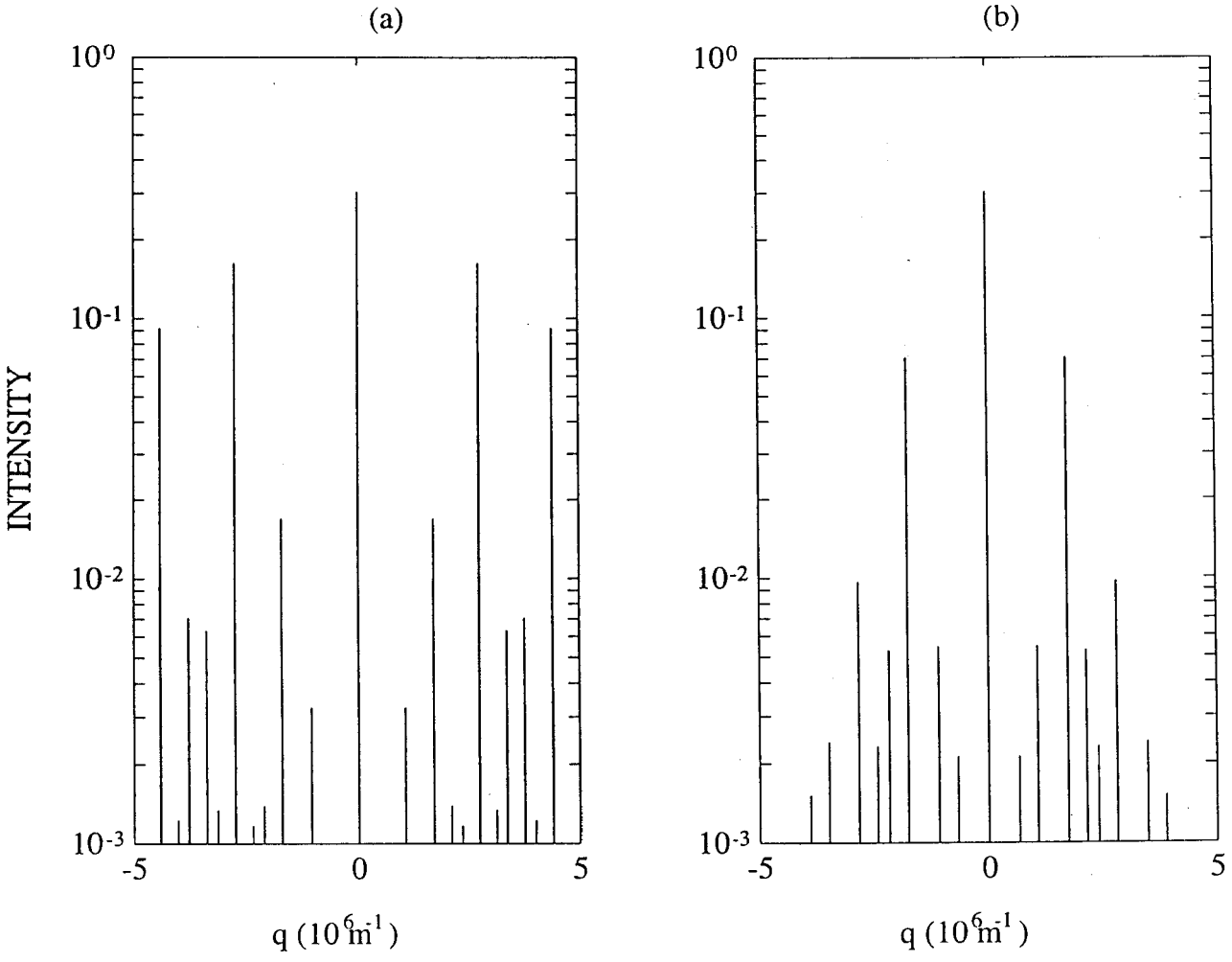

Figure B.2: The diffraction pattern for quasi-periodic amplitude gratings (a) for the sequence $S_1, D, S_2, D, S_1, D, S_1, D, S_2, \ldots$ (b) for the sequence $S_1, D_1, S_2, D_2, S_1, D_1, S_1, D_1, S_2, \ldots$.

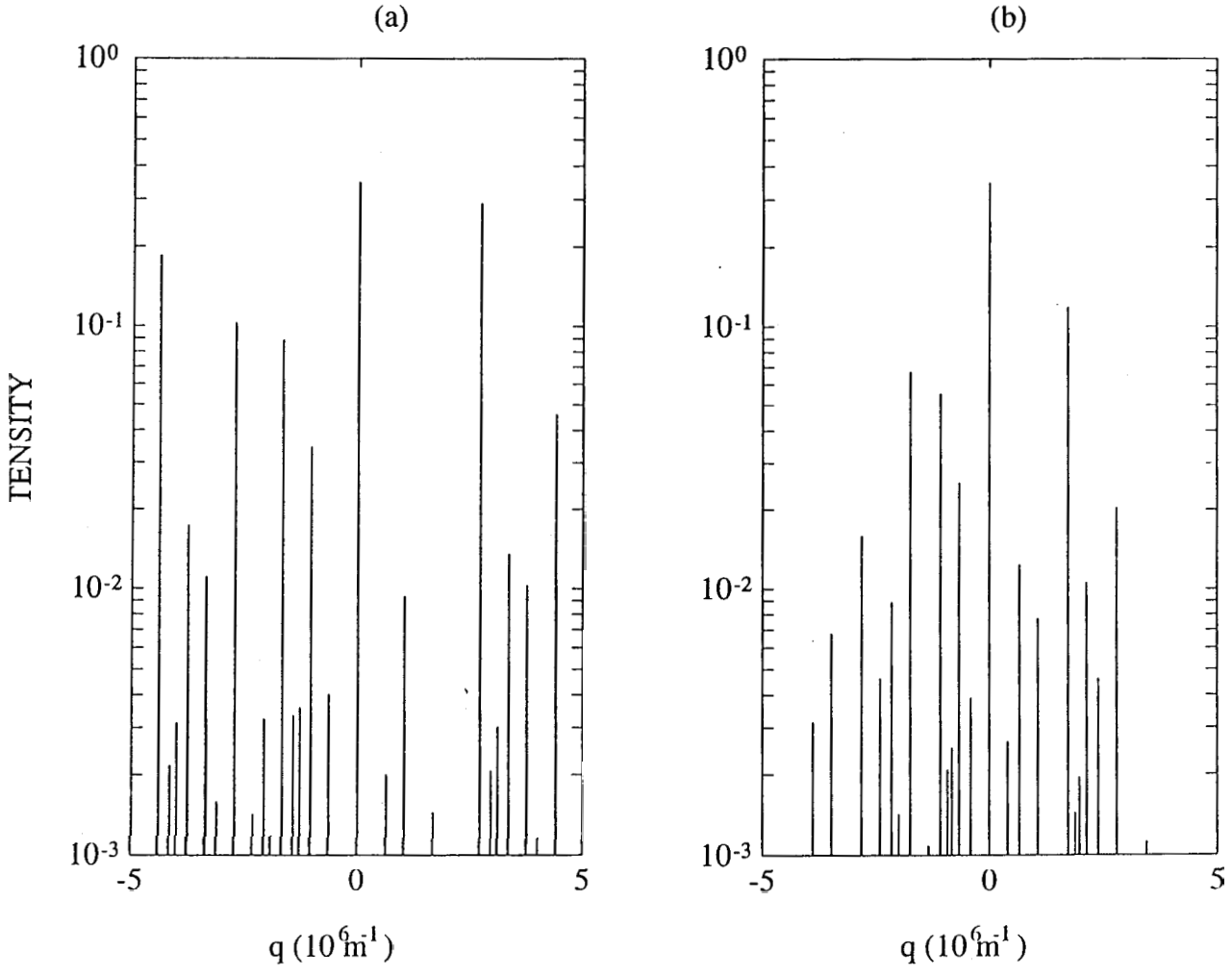

Figure **B.3** : The diffraction for the same gratings as given in figure B.2 but with the slit S_2 acting as an absorbing element.

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