MEASUREMENT OF SURFACE STRAIN BY SURFACE
REFLECTION RAMAN SCATTERING

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My talk today sort of comes from the unreal side of the world in the sense that this method of nondestructive testing is quite new and nobody has used it, and I am presenting this method as a possible method for the future. Of course, the unreal world today often becomes the real world tomorrow, so there is a good possibility that the method that I present here will become a useful one. At the moment, of course, the equipment that I use for these measurements can't be hung on the airplane wing or anything of that sort.

Let me explain what I do. What I do is inelastic scattering of light. Figure 1 shows a schematic of the experiment, with the sample surface indicated. I shine a laser beam, focus it down to the surface and then I look at the scattered light coming out of the surface. The sample can be a metal, an ideally semiconductor surface or an opaque surface. Then I collect the scattered light and analyze it, using a double grating spectrometer. I analyze the spectrum intensity versus the frequency shift from the laser, and what you see in this kind of spectrum is the scattering from the optical phonons. The phonons coming from the laser get inelastically scattered by the phonons that are thermally created inside the sample. Thus, the phonons coming out of the laser can either gain or lose energy. Here ω_0 is the laser frequency and ω_s is the scattered light frequency. So, by measuring the difference in frequency you can determine the frequency of the scattered waves. In this case, the scattering phonons are near the surface, because the skin depth or the penetration depth of the laser beam into the sample, into materials such as metals or some of the III-V semiconductors, is very short, like 1000 Ångstroms.

What you see is the condition of the material near the surface within the first, say, 2000 or 3000 Ångstroms, and the information that you can get from Raman scattering is, first the frequency of the phonon (from looking at the frequency difference, the loss or gain of the energy) and then also you gain information about the symmetry of the excitations (from looking at the polarization characteristics). For instance, if you have a single crystal material, your scattered light may have only one polarization. By looking at the linewidth, you can say something about the surface strain, and that is the subject that I want to discuss today.

From this you can see that the kind of information you can get is quite limited in a sense, because you can't see deep into the material as long as you use a visible laser, especially in materials that are of most interest, namely, metals. But that disadvantage can work to your advantage also, that is, if you are interested in just what is going on near the surface. Of course, cracks may occur inside, but corrosion, for instance, or oxidation occurs from the surface, so that you can detect just the beginning of whatever is going to happen (starting from the surface) by this method. Another advantage

RAMAN SCATTERING FROM SURFACES

$$\omega = \omega_0 - \omega_S$$
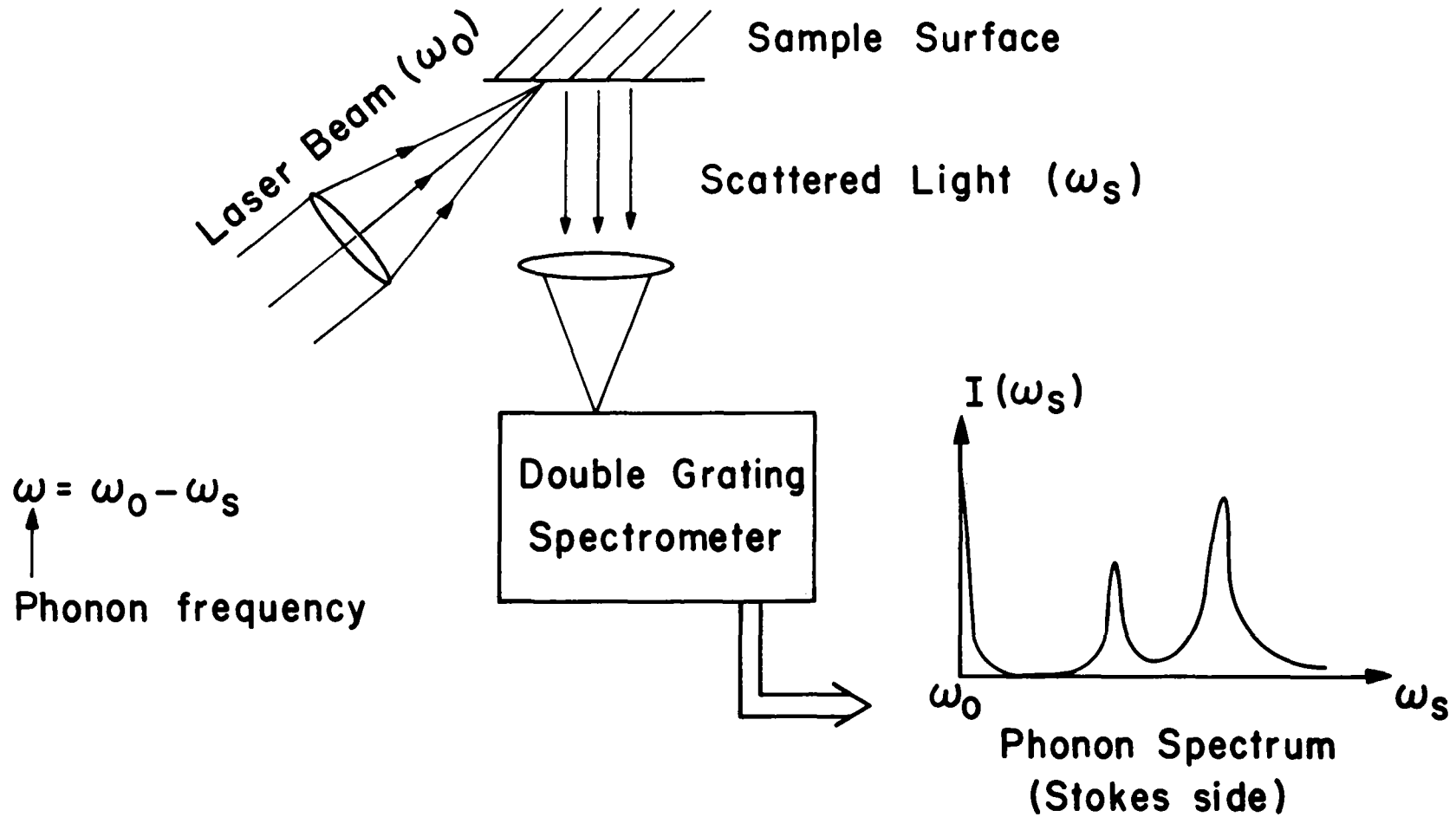
Phonon frequency

Fig. 1.   Schematic diagram of the Raman scattering experimental arrangement.

is that all you need is an optical access to the sample. You don't have to attach anything to the object that you want to study, and you can, by measuring the line-widths, measure what kind of strain exists in the sample. You can create a calibration standard that people have been talking about. Although at the moment this method is not used, I think this method would be very useful in determining the nature of defects that start the failures of materials.

For the sake of concreteness, consider Fig. 2. This figure shows the schematic diagram of what happens if the sample surface is free of strain. These are not the real data; these are exaggerated for illustration purposes. The phonon spectrum has a narrow line width, while for the strained surface the line width gets wider. By calibrating or correlating the amount of strain and the linewidth you can tell what sort of surface strain you have.

Figure 3 shows a system that I use which is somewhat impractical as far as a testing procedure goes. The scattered light is collected and analyzed using photon counting electronics and eventually you get the spectrum out. This figure shows the geometry of scattering and indicates that all the scattering occurs within the penetration depth of the laser beam near the surface, and this value, δ, is a few thousand Ångstroms at most.

Figure 4 shows the actual data for the case of GaAs. The top curve is the spectrum from a polished surface, and the next one is for the same surface etched, and the next curve is after that polished surface was annealed at some temperature for some fixed length of time. The bottom curve is the spectrum from a cleaved surface. You notice that the polished surface has much wider phonon peaks than all the others, while the cleaved surface has a very narrow phonon peak in comparison with the others. This should give you an idea of what we are measuring. What we are trying to do is to correlate the phonon linewidth with the amount of strain near the surface. If we can measure the line width for a known strain, then we can go back and calibrate how much strain there is for a given surface when the Raman spectrum is measured. That is the idea. We have tried various methods of controlling what we see. There are many ways: polishing, etching, annealing and cleaving.

It appears that when you polish, you damage the surface quite a bit. That is, when you polish, what you are doing is rubbing something hard against that surface and breaking pieces off. When you etch, you are chemically taking away atoms from the damaged surface, and eventually if you etch deep enough you get to the region where there is no strain. Annealing allows the atoms to rearrange themselves, to go back to a defect-free state, and, of course, a cleaved surface--well, there is no obvious reason why a cleaved surface should be that clean, but it is.

Figure 5 shows the temperature dependence of the phonon line width. Phonon line widths can be wide for various reasons, and this measurement was made to see what causes the phonon broadening in, say, polished surfaces. One of the possibilities was that phonons scatter from defects or scratches near
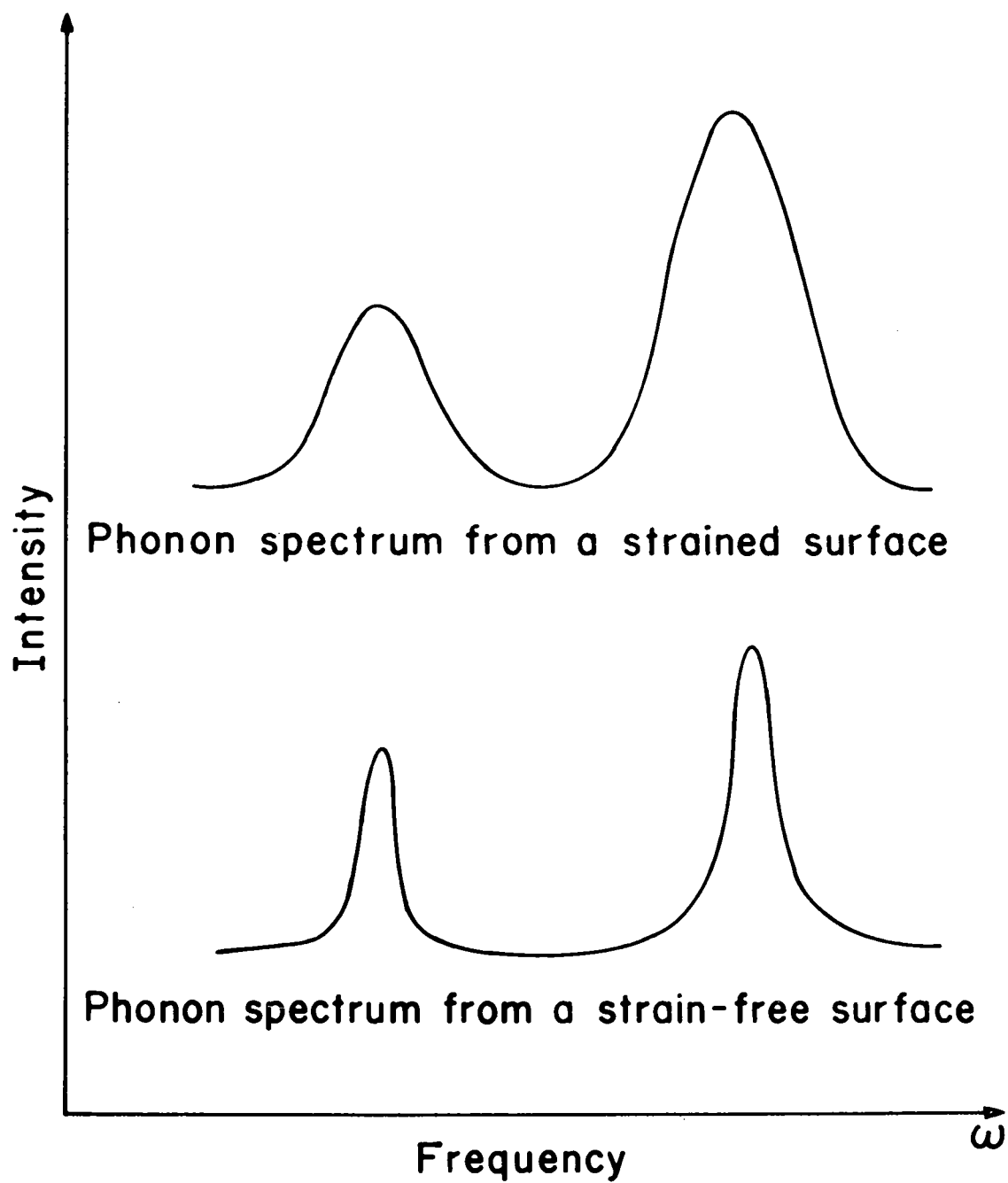
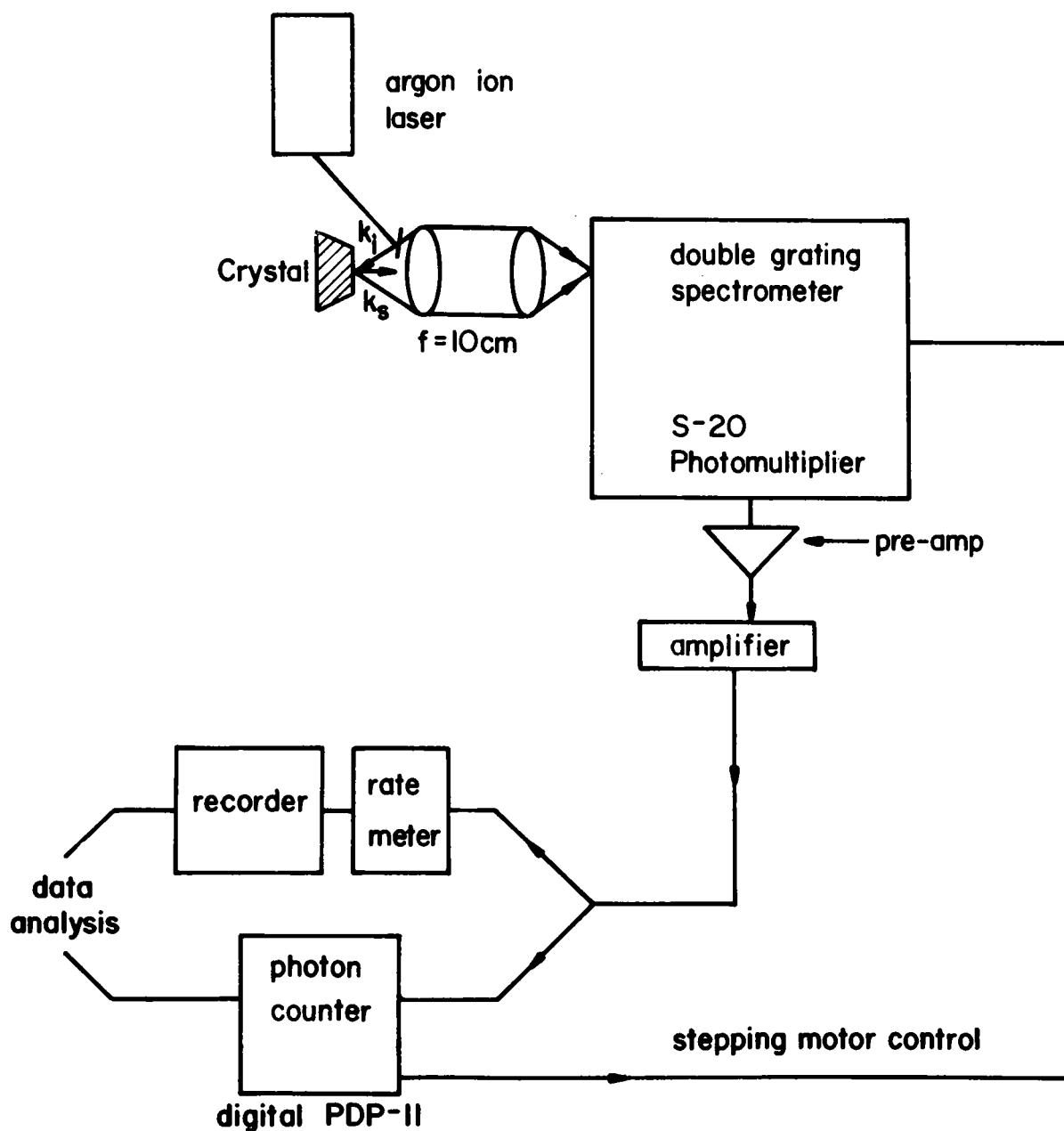Fig. 2. Schematic diagram indicating the phonon spectrum broadening resulting from surface strain.

argon ion
laser

Crystal

k_i

k_s

f = 10 cm

double grating
spectrometer

S-20
Photomultiplier

pre-amp

amplifier

recorder

rate
meter

data
analysis

photon
counter

stepping motor control

digital PDP-11

Fig. 3. Diagram of the instrumentation used for the Raman scattering experiment.
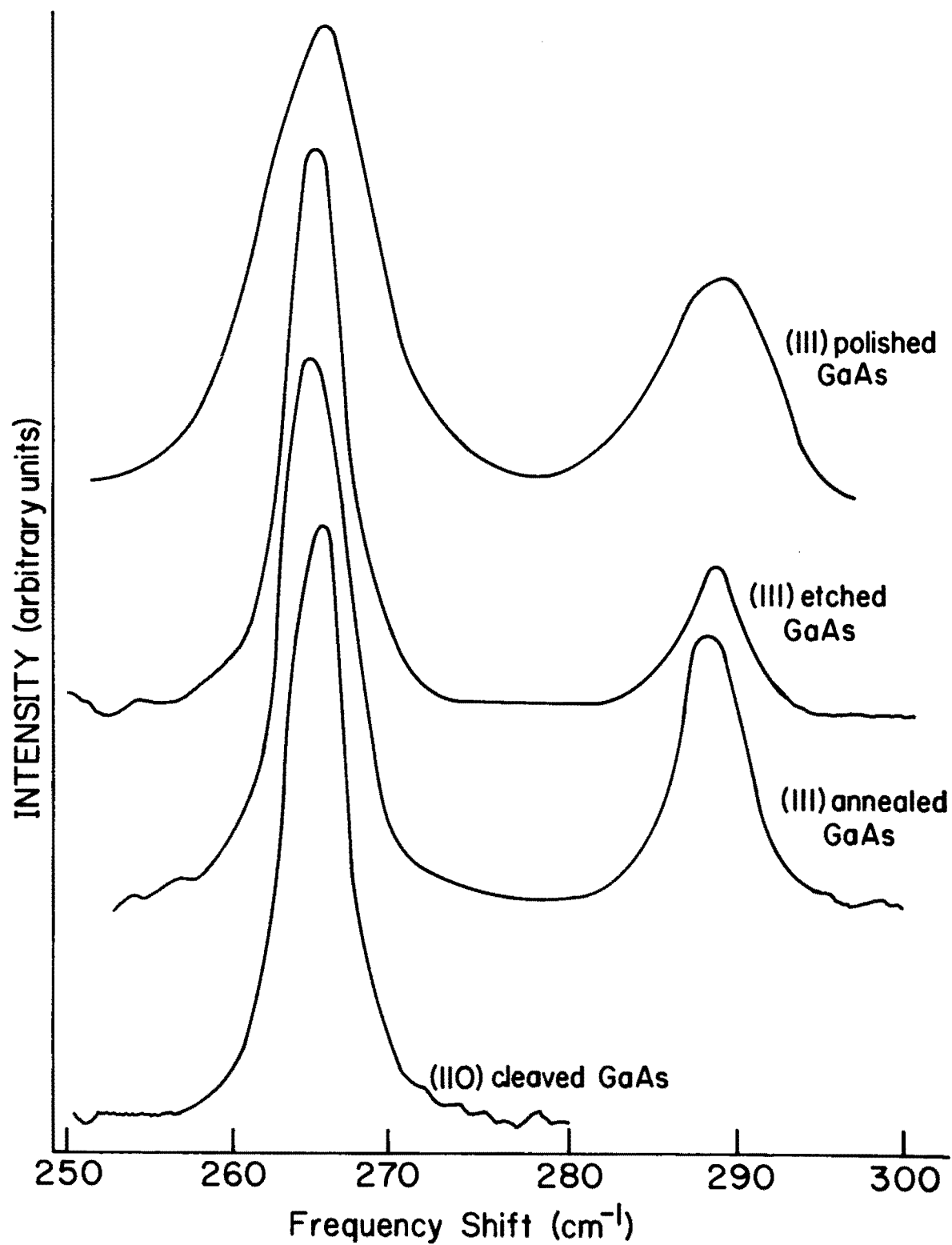
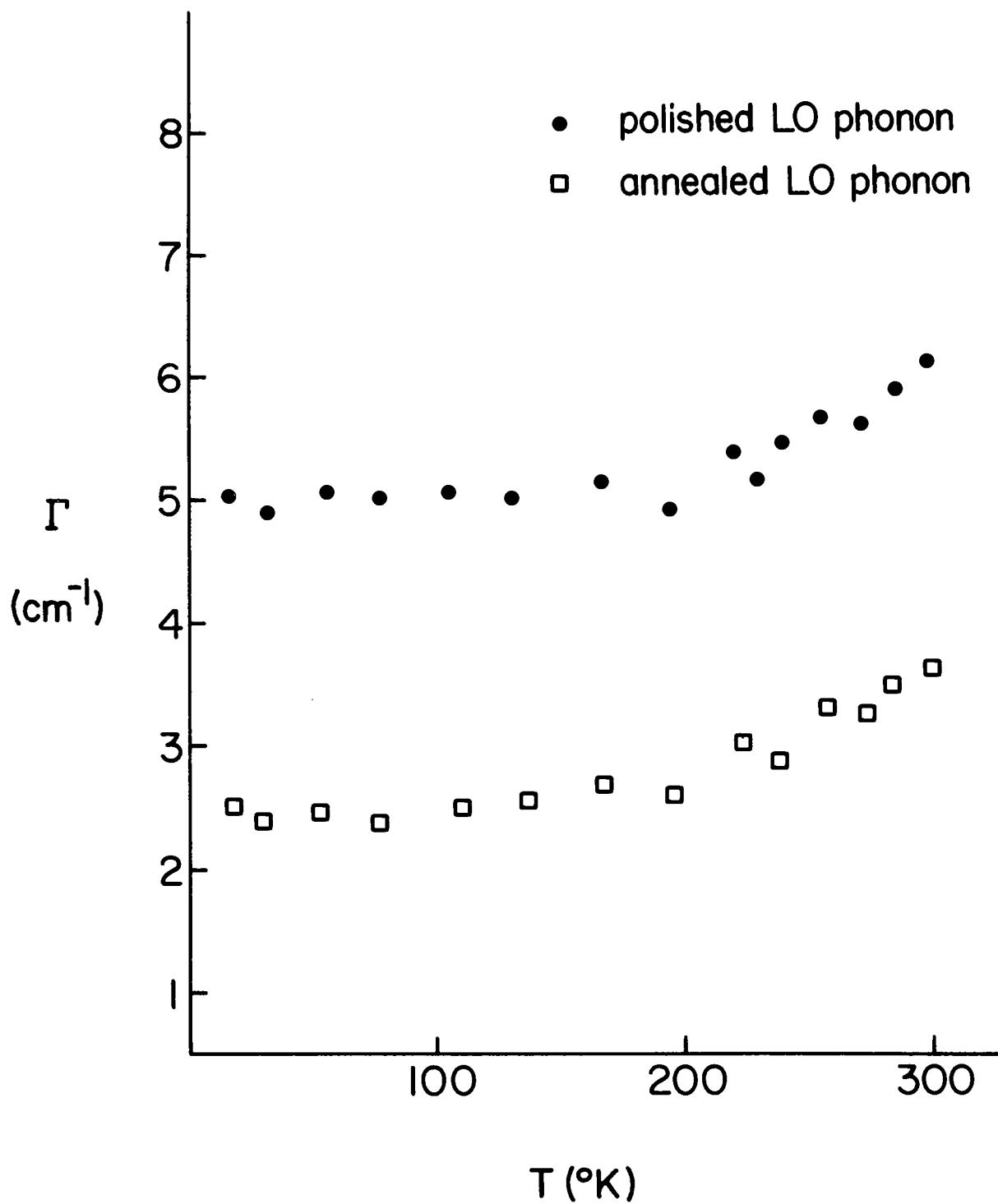Fig. 4. Raman scattering data for GaAs with various surface conditions.

Fig. 5. Temperature dependence of the phonon line width for polished and annealed surfaces.

or on the surface, and we thought that could be the cause. That's why we made this measurement, but it turns out that the difference between a polished surface and the annealed surface, the line width difference, is constant with the temperature. That showed that it is not the scattering but rather the inhomogeneous strain.

What happens is the following: in a strain-free crystal you have a certain phonon frequency. Then, if you strain the crystal, the phonon frequency will shift. If you compress it, the frequency will go up. You can sort of intuitively feel that, because if you squeeze a crystal it gets harder to squeeze further. If you stretch the crystal, the phonon frequency will go down and the different regions on the surface have different amounts of strain. For instance, if you have a groove, a different amount of strain is distributed around the groove, so that the phonon frequencies at different parts are different. We determined that was the cause for the broadening.

Figure 6 shows the line width dependence on the polishing powder size. The line width is on the vertical axis and the polishing powder size is on the horizontal axis. You find that as the polishing powder size goes up, the phonon line width increases. The laser frequency is fixed, so that the depth in which I am probing is constant. If you have a larger powder particle size to scratch off the surface, you are damaging into deeper and deeper regions, and that is what this diagram shows.

Figure 7 shows a correlation between the polishing powder size and the skin depth. If you change the laser wave length, the penetration depth changes. This figure is for GaAs, and the penetration depth for the shortest wavelength in this case, I believe, is 4880 Å. The line of an argon ion laser is approximately 1200 Å and for the short wavelength band, the penetration depth, δ, that was shown in the previous figure, is about 700 Å. So, for polishing powder of 1 μm size you notice that if you probe deeper and deeper, the phonon line width is constant. That is because damage is constantly deep into at least 1 μm. On the other hand, if you look at the cleaved surface, you notice that the phonon line width decreases as you probe deeper into the sample, that is, if you go into the bulk undamaged region. This method allows you to look at the distribution of surface strain as a function of depth.

An interesting case is shown in Fig. 8. This is data for InAs where the skin depth is much shorter for the argon laser lines that we produce and, of course, the polishing powder size is sort of fixed. We look at different depths of probe. You notice for the 0.3 μm polished surface the strain seems to be constant across between, say, 200 Å and 400 Å depth, but if you go to an etched surface or smaller polishing powder size or cleavage, you notice the amount of strain increases as you go into the bulk. Of course, I am talking about the first 200 or 300 Å. This is understandable, because if you polish or cleave and damage the surface, then the free end of the surface, namely, right inside the surface, can relax. On the other hand, the intermediate region has a hard time relaxing so we are, right now, extending this by using a dye laser, so that we can have variable skin depths. We expect that this line width will increase and then come down into the strain-free value. That's the kind of thing that we are doing now.
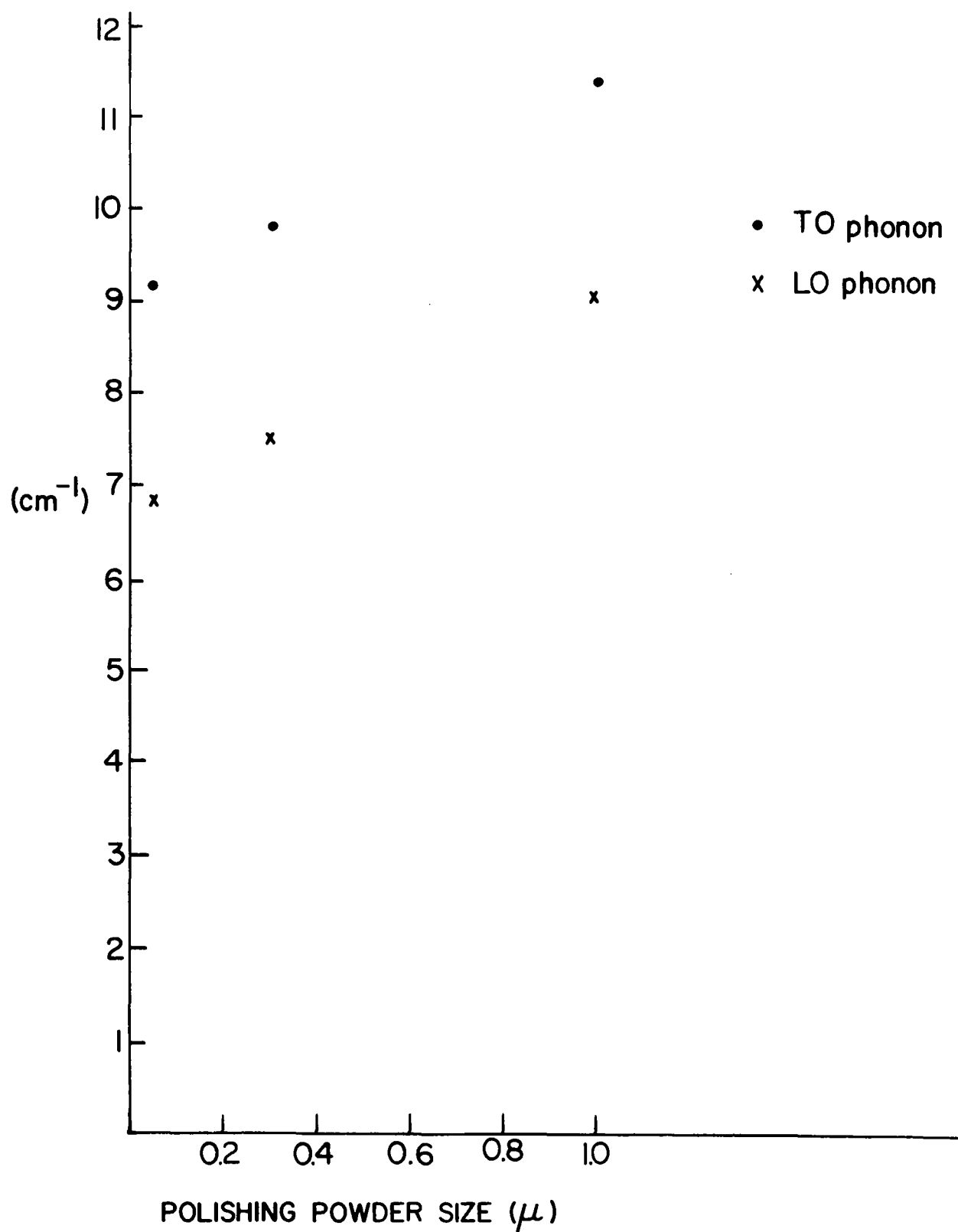
Fig. 6.   Influence of polishing powder particle size on phonon line
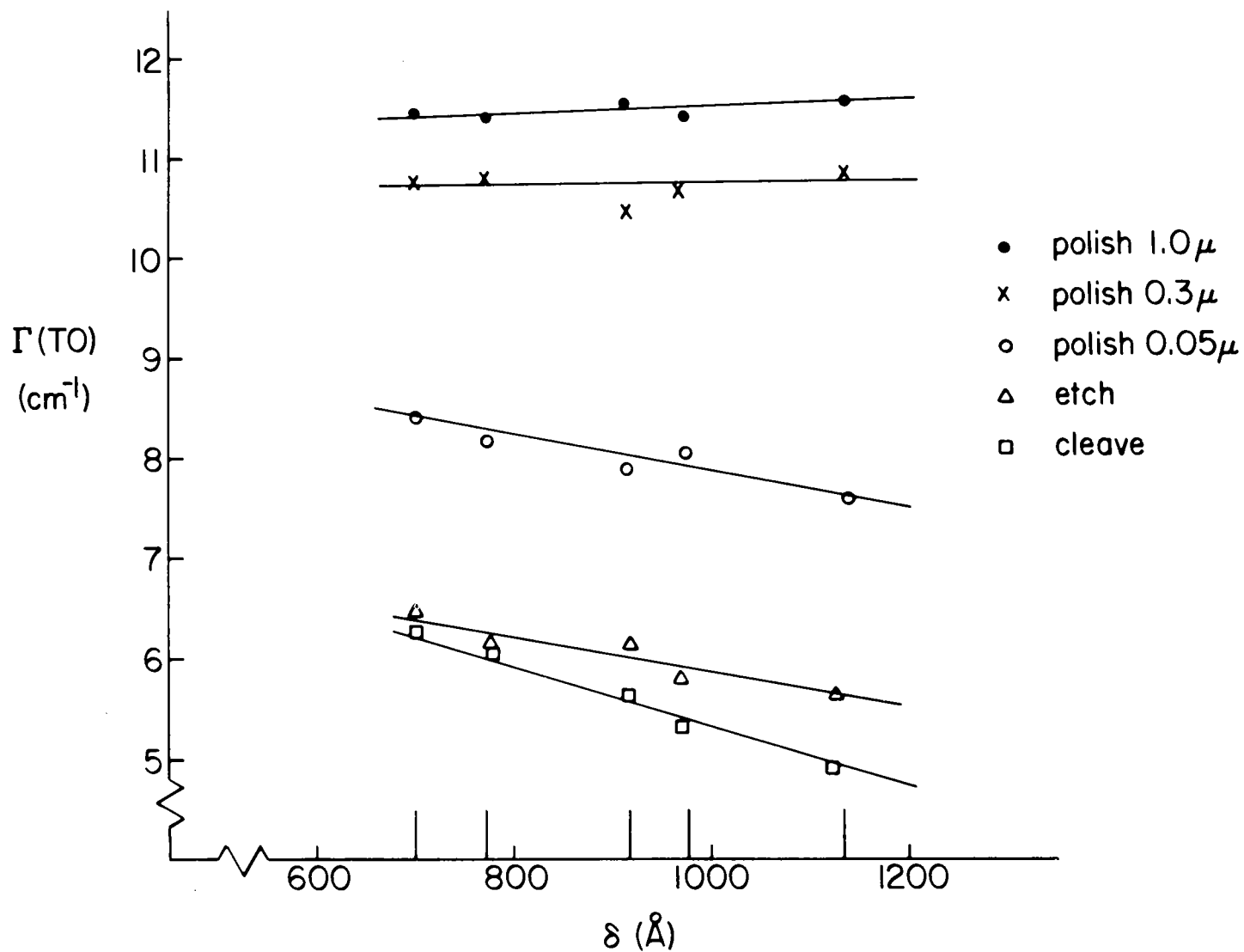width for a polished surface.

Fig. 7. Phonon line width as a function of penetration depth for several surface conditions.
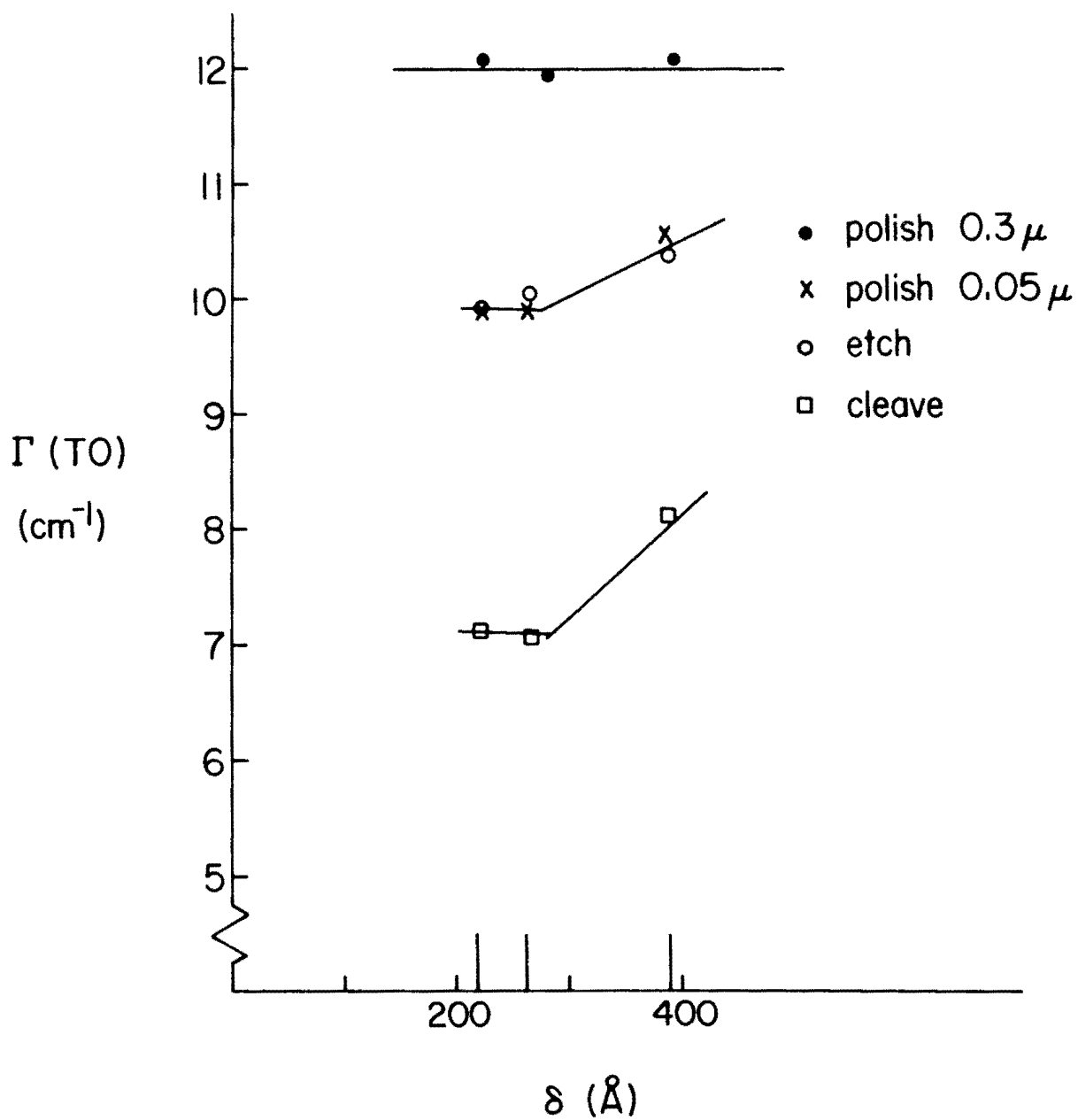
Fig. 8. Phonon line widths vs penetration depth for
InAs with several surface conditions.

Figure 9 shows the annealing characteristics. For practical purposes, you can assume the line width, Γ, represents some indication of the amount of strain in the surface. Thus, if you anneal (annealing at $200°C$ in this case), you notice the line width decreases as you spend up to about 2 1/2 hr., and then eventually it will come to an equilibrium, and this is approximately the same as we get for the cleaved surface. So, the polished surface had lots of damage, and then by annealing you could eliminate some of the damage.

In any case, we have correlated the line width with the experimentally obtained value of breaking stress, and they correlate very well. People measure the phonon frequency shift due to stress, and there, you know, you can give a known amount of stress. In the case of GaAs the breaking stress is something like 6×10^9 dyn/cm^2. This corresponds to a broadening of the phonon line of about 3 cm^{-1}.

In conclusion, what can we learn from this method? Well, we can measure the magnitude of the surface strain and monitor the amount without touching the sample; and we can measure the distribution of the strain, as a function of the depth from the surface. This kind of capability can be quite useful in many of the semiconductor and metal devices whose performance depends on the surface, like metal oxide semiconductor devices or integrated optics where very thin films of semiconductors are used. Another great advantage about this is that the locality at which you are making the measurement can be defined within, say, 10 μm because the size of the laser spot can be made that small, and you can readily check the amount of surface strain at each spot with a resolution of, say, 10 to 100 μm. We have used this method to study surfaces of semiconductors with ion implantation and also we have studied GaAS films. Here again, the kinds of modes that you see in Raman scattering reflect the condition of the interfaces and the thickness, uniformity and single crystallinity of the film. Hopefully, this method can be used for structural materials as well, once we get used to this idea.
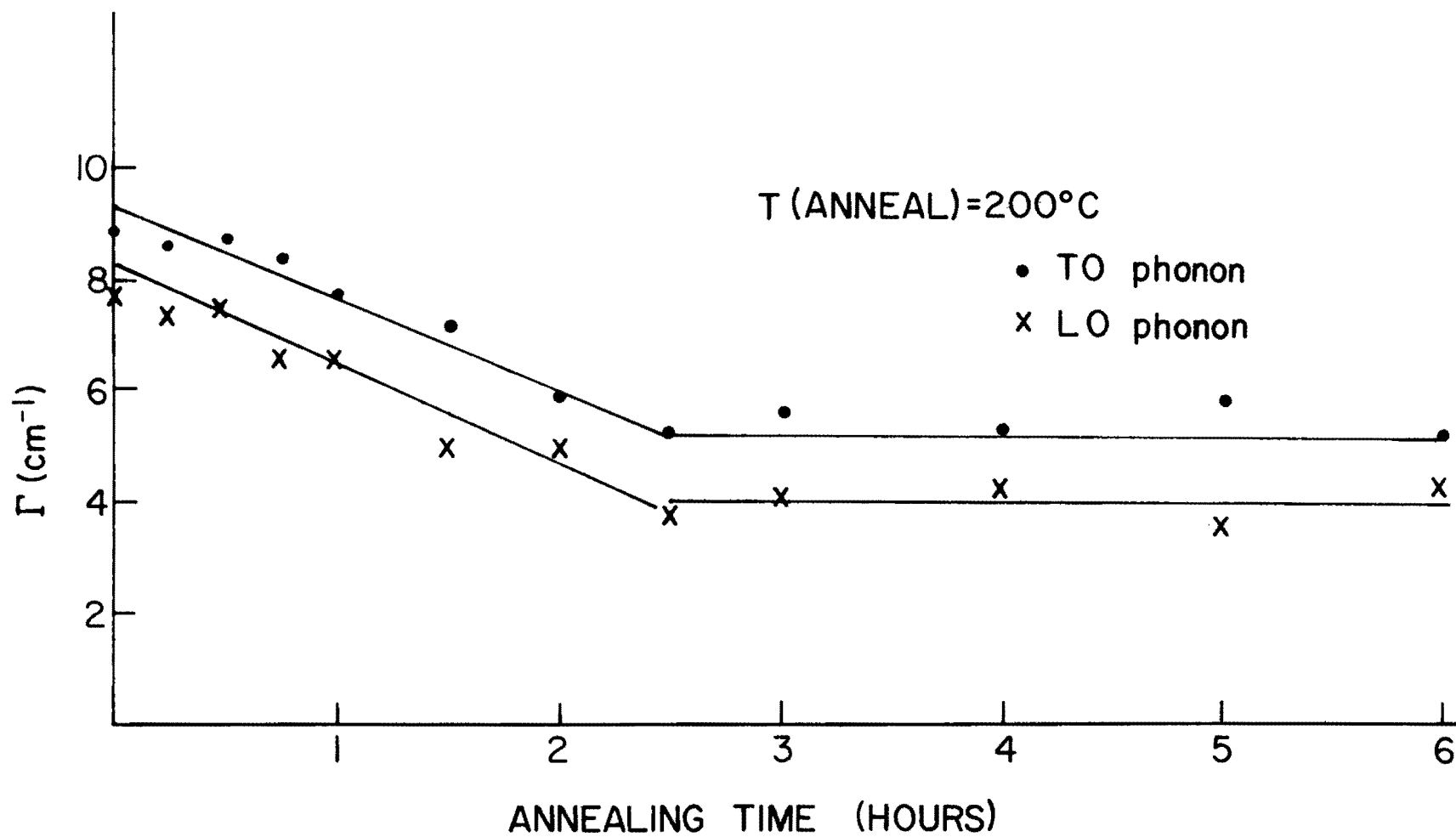
Fig. 9. Influence of annealing on phonon line widths.

DISCUSSION

DR. BILL WALKER (AFOSR, Washington): We have a question.

DR. SY FRIEDMAN (NSRDC, Annapolis): If I may ask a couple of questions, have you ever tried a direct experiment where you impose, shall we say, a stress or strain on the specimen while this measurement was being made, and measured the broadening that you predict or, perhaps a decrease in the broadening?

DR. USHIODA: No, I haven't performed that experiment, but other people have done that. Actually, what you see is a shift in frequency.

DR. FRIEDMAN: The point is, you are using this...basically somebody else is measuring a change in the phonon frequency --

DR. USHIODA: Yes.

DR. FRIEDMAN: --associated with the crystalline stress, and you are using that to interpret your experimental results?

DR. USHIODA: Yes.

DR. FRIEDMAN: Okay, I am very much interested in residual stress measurements, so if you will bear with me for just another minute. The other question is: did you find any directional dependence in terms of the way the azimuth line, if you will, of the laser beam is set with respect to the surface normal? Strain is a tensor, it is not a simple scaler and, as a matter of fact, normally one just measures the component of the strain associated with a certain directional space in that direction.

DR. USHIODA: Right.

DR. FRIEDMAN: That wasn't brought out in your presentation at all.

DR. USHIODA: Yes, you are right. No, we haven't measured any directional dependence and I don't think it is possible using this method unless we do things like polish a surface with motion in only one direction, say, and then look at it from different directions.

DR. FRIEDMAN: See, we measure residual stress in welds and people are very much interested in whether the residual stress is large along the axis of the weld or at right angles to the axis of the weld. That makes a difference.

DR. WALKER: If you were to do that, not at a point in terms of a tensor point function, but over a gauge length--say, you have a point layout of an orthogonal reference axis, then would you be able to make measurements, say 1/2 inch apart, at three points?

DR. USHIODA: You look at this point and that point and that point and compare the strains.

DR. WALKER: Right, and get an approximation to the strain.

DR. USHIODA: That would give you the strain gradient, but not the direction of the strain, I'm afraid.

DR. FRIEDMAN: Well, the point that I'm trying to make is really before you can have a complete measurement you need the components of the strain tensor, if you will.

DR. USHIODA: Yes, that's true.

DR. WALKER: Another question here?

PROF. ROBERT FRANCIS (University of Illinois): When you switched from, what was it, (111) cleavage to (110), or something like that--

DR. USHIODA: Yes.

PROF. FRANCIS: --you must have lost one line --

DR. USHIODA: Yes.

PROF. FRANCIS: -- due to polarization?

DR. USHIODA: Yes.

PROF. FRANCIS: And the other line got narrower, right?

DR. USHIODA: Right.

PROF. FRANCIS: In a sense it is a different direction of observation.

DR. USHIODA: Yes, but that is not the same thing as that gentleman mentioned. That is, the direction of strain inside a surface maybe that way or this way. Isn't that what you asked?

PROF. FRANCIS: You are now looking at the --

DR. USHIODA: That is a completely different surface. I'm looking at only the first thousand Ångstroms of this side and that side.

PROF. FRANCIS: I said, in a sense.

DR. USHIODA: Yes.

PROF. FRANCIS: It is a polarizability tensor that you are looking at, in effect. That is what your magnitude purports, and there is no reason to believe that it is isotropic.

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DR. USHIODA: No, it is not isotropic, we know that.

DR. ROGER DEWAMES (Rockwell International Science Center): Have you performed any experiments on metals?

DR. USHIODA: No. There are cases like $AuAl_2$ and $AuGa_2$--some of these methods have been measured and people mentioned that the line width comes out somewhat random, and as we look back we know why. Some of the measurements were done on natural surfaces of a single crystal and some were done on polished crystals.

DR. DEWAMES: One more comment on this. In metals, most simple metals like aluminum, there is no optical branch.

DR. USHIODA: No, that is a problem with aluminum and such metals. You would have to go to things like bismuth or zinc. We need at least two atoms per unit cell.

DR. DEWAMES: I hope you are not suggesting that we make the B-1 out of bismuth and zinc.

DR. WOLFGANG SACHSE (Cornell University): What counting rates are involved in these measurements?

DR. USHIODA: Let's see, I think typical counting rates of photons are about 20 to 30 or something of that order with 400 milliwatts going in from the laser.

DR. SACHSE: That is with a 1 wavenumber resolution?

DR. USHIODA: Approximately 2 wavenumber resolutions.