The Effect of Surface Roughness on the Frequency of Surface Plasmons

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The theory of photoemission from metals is still in the state of development. There are relatively few rigorous calculations of photoemission spectra from metals. Much of the work which is being done currently is addressed to the question of the role of many-body interactions in this type of problem, and it is, indeed, a theoretical question on ideal metal surfaces of considerable complexity. The introduction of surface roughness requires a model theory, and it requires some model concept. Now, the thing I am going to address myself to in this talk is to the role of surface plasmons in enhancing the photoemission of metals.

As shown in Fig. 1, a surface plasmon is essentially an electromagnetic wave which can exist on the surface of the metal and which is exponentially damped with distance away from the metal surface. This surface electromagnetic wave is obtained by solving Maxwell's equations for a metal dielectric interface. When you do that, you obtain the dispersion relation of Fig. 1, which describes how the frequency varies with wave number for the surface plasmon. The electric field accompanying the surface plasmon can propagate along the surface with a velocity which is determined by this dispersion curve. The wave is exponentially damped with depth away from the free surface. The upper part of Fig. 1 shows the nature of the electric field lines. If you were to imagine charges distributed along the surface (positive and negative charges along the surface) then the electric field lines would have this type of configuration.

The condition for the existence of plasmons which I will be talking about later on is obtained by equating the real part of the
Fig. 1. ELECTRIC FIELD AND DISPERSION CURVES FOR SURFACE PLASMONS GENERATED ON A ROUGH SURFACE
dielectric function of the material to minus one or to the dielectric constant of the surrounding dielectric material.

Now, what I am going to be talking about is the asymptote on the dispersion curve. The plasmon edge in aluminum is 10.6 electron volts. That number is called the plasmon edge. Photoemission from a metal begins at the photoelectric threshold, and as you increase energy towards ultraviolet region, you approach the plasmon edge beyond which the photoemission is greatly reduced.

Now, if we look at the effect of surface roughness on photoemission, and taking the experimental results of Endriz and Spicer, we have the following kind of experimental situation. Figure 2 is taken from the paper of Endriz and Spicer. What they were looking at is specimens of aluminum which we would call nearly perfect. The largest fluctuation or mean square deviation from flatness was about 25 angstroms on the roughest one of the samples. Now we are plotting here yield in electrons per incident photon versus photon energy. Energy \( \sqrt{\hbar \omega_p} \) over the square root of two is about 10.6 electron volts and corresponds to the flat asymptote that is shown in Fig. 1. Now notice from Fig. 2 that as we go to rougher and rougher specimens, the yield curves are both increasing in magnitude (that is, we are getting more electrons out of the material) and there is a shift to lower photon energies.

In the Endriz and Spicer theory of surface roughness enhanced photoemission, the picture that they present is that the plasmon edge, namely, the 10.6 electron volts for aluminum, is not changed by surface roughness. Surface roughness permits plasmon-photon coupling. If you have an ideal metal surface and an electromagnetic wave incident on that surface, it doesn't couple to the plasmons at all. It doesn't excite the plasmons. In order to excite the plasmons, you either have to have surface roughness or some other type of perturbing element present. Roughness provides the perturbing element and permits the coupling to the plasmons. Plasmons carry with them an electric field, an electric energy density; so, in addition to
Fig. 2. EFFECT OF SURFACE ROUGHNESS ON THE YIELD OF PHOTOELECTRONS
(σ MEASURES THE RMS SURFACE ROUGHNESS)
AFTER ENDRIZ AND SPICER
the electric energy density of the incident electromagnetic wave, there is an additional electric field energy density associated with these plasmon modes that are excited. This additional energy results in kicking additional electrons out of the metal.

Now, the reason that roughness moves the yield to lower photon energies here in this particular picture is essentially not because the plasmon edge is changing, but that you are simply coupling to plasmons which are lower down in the retardation region. Remember the dispersion curve of Fig. 1. There is a whole range of K vectors that the dispersion curve describes, and as you go to increasing roughness, you can couple to plasmons that are further down on the dispersion curve.

So, one of the things that I wanted to look at was, what is the effect of an arbitrarily rough surface on the plasmon edge itself? How can we look at that in a very simple way? Let's see where this $h\omega_p/\sqrt{\varepsilon}$ comes from.

For an ideal vacuum-plasmon interface the plasmon dielectric function is $\varepsilon_p(\omega) = 1 - \omega_p^2/\omega^2$ where $\omega_p$ is the plasmon frequency and $\omega_p^2 = \frac{4\pi n e^2}{m}$. Treating the electric field as a quasi-static field neglecting retardation and applying a boundary condition which says that the normal component of electric displacement across the boundary has to be the same in both the plasma and vacuum, gives $\varepsilon_p(\omega) = 1$ or $\omega = \omega_p/\sqrt{\varepsilon}$, which, in the case of aluminum, gives 10.6 electron volts. If you were to replace vacuum with a dielectric then the plasmon asymptote is given by $\omega = \omega_p/\sqrt{\varepsilon_d}$.

So, the next calculation we can do is to see what curvature has to do with this 10.6 electron volt number, and that is to look at a cylindrical plasma.

Consider a cylindrical plasma of radius R. We use a potential which is a circular harmonic inside and decays as 1/R outside. We equate the electric displacements across the boundary, again obtaining a plasmon dispersion relation $\omega = \omega_p/\sqrt{\varepsilon}$ equal to 10.6 electron volts (in the case of aluminum). This is the same result obtained for the plane.
Now, notice that both the cylinder and the plane have something in common. They are both surfaces of constant curvature. Let's look at an ellipse. In the case of an elliptical plasma cylinder we get a new dispersion relation \( \omega^2 = \frac{\omega_p^2}{1+e_\text{d}} \coth \alpha \), which shows that the plasmon edge is now shifted. It now depends on the hyperbolic cotangent of alpha, where \( \coth \alpha = (1-e^2)^{-\frac{1}{2}} \), and \( e \) is the eccentricity of the ellipse. For a circle where the eccentricity is zero, we recover \( \omega = \frac{\omega_p}{\sqrt{1+e_\text{d}}} \). In the case of a very flat ellipse with very sharp edges on it, we see that this plasmon edge is radically perturbed away from the value for a circle or for an infinitely long plane.

The next question then is how do we treat this problem in a very general way. Well, suppose we talk about a completely arbitrary surface with arbitrary curvature. Suppose we have a completely arbitrary surface. You can have all kinds of roughness on it. What do we do with that? Well, the thing that we do is to produce a logarithmic potential \( \phi(x,y) = \int_0^L \frac{R(s)}{\log(R)} \, ds \). Here \( R(s) \) is a local charge density per unit of surface area in the cylinder and \( R \) is the distance from a point on the surface to some point in the interior. Remember from potential theory that a logarithmic potential automatically satisfies the condition that the potential inside the plasma and outside the plasma is continuous. So, all we have to do is equate the gradients, properly multiplied by the dielectric constants, to get the corresponding dispersion relation.

The solution of this problem, as you recall from the theory of potentials, yields an integral equation for a whole set of plasmon frequencies \( R(s_0) = \lambda \int_0^L k(s_0,s)R(s) \, ds \) instead of a single dispersion relation. This is a homogeneous Fredholm integral equation. It has an eigenvalue parameter, \( \lambda \), involved in the plasmon dispersion relationship in the following way:

\[
\lambda = \frac{\varepsilon_p - \varepsilon_d}{\varepsilon_p + \varepsilon_d} ; \quad \omega^2 = \frac{\omega_p^2}{1+e_\text{d}} \left( \frac{1}{\lambda - 1} \right),
\]

in which \( \varepsilon_p \) and \( \varepsilon_d \) are the dielectric constants of the plasma and the dielectric respectively. The diagonal part of the kernel, \( \hat{k} \), of this integral equation is the local curvature at each point of the boundary of plasma.

So, what we have learned by this analysis is that the plasmon edge,
i.e., the asymptote in Fig. 1 is, in fact, a function of the curvature on the surface. If you have an arbitrary surface the plasmon edge is obtained by solving a Fredholm integral equation. You can solve this in the case of an ellipse, exactly, and if you do that, you get a whole set of asymptotes. There is a lowest one; it is \[ \omega^2 = \omega_p^2 / l + \epsilon d (1 - e^2) \] in which \( e \) is the eccentricity.

There are higher modes, too. Physically, to what do those modes correspond? If you think now of a wave going around the surface of the cylinder, then it is easy to see that there is a quantization condition. You have to have an integral number of wave lengths for that wave in order for it to run around the cylinder even though it is exponentially attenuated with respect to depth as you go into the plasma. It is those sets of modes that are the plasmon eigenfunctions. They are obtained by solving the integral equation. The charge density \( R(s) \) gives you the variation of charges, both plus and minus, around the cylinder. The lowest order eigenfunction would have all pluses on one-half of the cylinder and all minuses on the other half of the cylinder. As you go to higher and higher modes, you get more and more of these sign variations. That is what the eigenfunctions mean. The eigenfrequencies are the asymptotes of these dispersion relations.

References

DISCUSSION

DR. TENNYSON SMITH (Science Center, Rockwell International): The Spicer paper gives a theory for a very smooth surface which has very little roughness on it, and the theory is claimed by them to be limited to a certain roughness. Beyond that, it is not in effect. Now, what you have done is to try to broaden that in terms of going back to fundamentals to try to extend it to a much greater roughness. You are not limited to any particular roughness in the way you have gone about this?

DR. KRAUT: Right.

DR. SMITH: The second question is: If you have solved that kind of problem, are you to the point now that you can correlate your expressions in terms of some kind of roughness parameters of a given surface such as autocorrelation length and a mean distance roughness?

DR. KRAUT: Right. The answer to that question is, yes. The part that I didn't say was that the kernel in the integral equation that I wrote down is something which reduces to the local curvature at every point on the surface. If you have a statistical surface, then there obviously is going to be some statistical function $K$ that describes that surface.

So, you are going to wind up with solving an integral equation with a kernel which is described in a statistical fashion and its eigenvalues will have some statistical distribution. That's the thing you are going to measure.

DR. SMITH: If we were to give you a surface by scanning electron microscope or profilemeter or something, i.e., we actually give you a mean distance of undulation and autocorrelation, could you give us some pictures like you showed us?
DR. KRAUT: Yes. The crucial question is: Can you see a shift; do you have enough resolution in the experiments to see shifts in the plasmon edge away from 10.6 eV?

Suppose we talk about aluminum. Suppose we had aluminum samples of varying degrees of roughness and we were looking at those yield curves versus energy. Could you detect experimentally the change in the yield in that plasmon yield?

DR. SMITH: Well, I think in the picture you showed us, it had changes of about a factor of three produced by that very, very small roughness that they are talking about.

DR. KRAUT: Yes.

DR. SMITH: At this point you don't know what the magnitude would be from your equation--is that what you are saying?

DR. KRAUT: Well, I haven't solved that problem, but I assume that it would be fairly large.

DR. SMITH: In that case, experimentally you should be able to get it.

DR. KRAUT: You should be able to see it, right.

PROF. HENRY BERTONI (Polytechnic Institute of New York): This is sort of a two-part question. Is there a correlation between the surface roughness and the autocorrelation distance, and if there is, can you relate this shift back to thinking of a locally periodic surface so that as you raise the size of the roughness, you are increasing the period and, therefore, the coupling to the surface plasmon will occur at a longer wave length or lower frequency?

DR. KRAUT: Sure.

DR. WILLIAM SCOTT (Naval Air Development Center): You have established certain conditions on the dielectric constant under which these plasmons can exist. I am wondering if on a regularly rough surface you couldn't possibly optically determine whether or not these plasmons are being propagated by simply looking, say, at the
variations in the point at which your dielectric constant crosses minus one?

DR. KRAUT: Yes, as a matter of fact, these plasmon modes are of interest as a means of propagation on metal surfaces. There has been some recent work by people at Bell Labs, Barker, in particular, and people elsewhere on using prism couplers. I think they used calcium molybdate prisms to excite surface plasmons by placing the prism close to the surface and then coming in at a critical angle. You can actually excite these surface plasmons and you can detect them and you can use the dispersion to create very high frequency dispersion delay lines of various kinds. In an area which is completely apart from what we are talking about now, they can also be excited with grating couplers. Those experiments have been performed and seen and people have done these things.

DR. GERALD GARDNER (Southwest Research Institute): I would like to ask a couple of naive questions which I think go back to and may couple together all of the papers that we have had here on the whole area of emission of electrons from surfaces and effects thereon.

One of the questions is that there used to be the notion, and I felt that notion was expressed by Himmel, that it was possible to get the emission of electrons that are somehow related to metal deformation in the absence of light altogether, in total darkness. If you deform the metal, electrons would come out of the surface. I would like to ask, is there any quite direct, straightforward, no tricky kind of evidence that this is, indeed, the case? I will not accept as an argument something that for which chemistry can be an alternate explanation, namely, that you put a piece of photographic film against it, which obviously might get some effect that could be explained by other arguments.

What is there in the evidence that says there either are or there are not electrons that are emitted in total darkness that could be
attributed to some kind of mechanical effect in the material?

DR. KRAUT: I think some members of the audience may be better qualified to answer that particular question.

DR. GARDNER: I address it to anyone who knows anything about it.

PROF. L. HIMMEL (Wayne State University): I do not know of any evidence that emission can be observed under those circumstances from a clean metal surface in the dark when it is mechanically deformed; however, if you have an oxide covering on the surface, and in the case of aluminum, if you have a relatively thick oxide layer on the surface, then in the dark, and regardless of what atmosphere or environment you do this in, if you mechanically deform the metal, you produce cracks in the oxide, and the mechanical energy which is released at the tip of a propagating crack is apparently sufficient to cause emission of electrons from the surface. It appears that electrons in this case, however, are coming from the oxide and not from the metal, but there is an example of what might be called tribo stimulated electron emission. But I do not know of this happening in the case of a clean metal surface.

DR. GARDNER: The other question that I wanted to ask relates to explanations of this whole thing. If I understand your rather deep theory here, the ultimate explanation concerns the effect of fatigue on what we now simply call just the photo electron effect. There is no point in coining a neologism for something that has a standard. The effect of fatigue on the photoelectric effect is merely geometric. It is simply because the surface takes on a shape that it didn't have before and has nothing to do with mechanisms which couple vacancies in a complicated way to conduct electrons that come fleeting to the top and discombobulate someway.

DR. KRAUT: For this particular theory, that is correct; that's right.

DR. GARDNER: I would like to hear from someone who thinks he can defend
the converse point of view, that they must in some way be coupled to the motion of dislocations or vacancies or the like that takes place in a fundamental level on a fatigue mechanism.

DR. OTTO BUCK (Science Center, Rockwell International): Well, I am not a defender of that theory, it is one of the possible explanations. The Boeing people about seven or eight years ago did a series of experiments that were torsion experiments. I don't recall right now whether all of it was studied in a vacuum or not. Let's forget about that question right now. What they tried to do was they tried to correlate, for instance, the line energy of the dislocation with the energy coming out as exo-electrons. They had luck in some of their materials; in other cases, they did not. Why not, I don't know; nobody knows right now, but that is one of the objectives that we now have, i.e., to go through a couple of various different pure metals and study that systematically. That hasn't been done, to my knowledge. The Boeing people tended to say, "No, there is no correlation between the line energy of a dislocation and the release of an exo-electron from the metal surface."

DR. GARDNER: It is your opinion, then, that the issue has not been resolved in the prior research?

DR. BUCK: That is right.

PROF. HIMMEL: May I speak to that question? I agree that I don't think the question has been answered definitively, but on the other hand, I personally do not believe that vacancies play any major role in the process for a number of reasons.

In the first place, with respect to aluminum, the energy of formation of a vacancy in aluminum is less than 1 eV, and I don't see how this is anywhere near sufficient to stimulate the emission of electrons, either from the metal or from the oxide.

Secondly, there has been some recent Russian work which I am not really going to defend, but in which they attempted to measure the emissions from quenched metals. What they should have found if vacancies play a roll in the process is that they got greater emissions
from specimens quenched from the highest temperature which had the
greatest concentration of quenched-in vacancies which would then
migrate to the surface. What they actually found was exactly the
reverse, that the specimens quenched from the lowest temperature
gave them the greatest emission. I think the question is still up
in the air, but I personally would be surprised if--

DR. GARDNER: The evidence as you interpret it now is not in favor of some
complicated way in which a lattice defect, moving through the matrix
of the material toward the surface in some way couples to the electrons
and pop them out?

PROF. HIMMEL: No, you need additional stimulation, either photo stimulation
or other sources of stimulation in order to eject electrons.

PROF. PAUL FLINN (Carnegie-Mellon University): I have a related question.
If there is some complicated mechanism where extra energy is supplied
by some defect in the material, one might expect photo emission for
a light energy below the usual photoelectric threshold. Has anybody
looked?

DR. SMITH: The answer is no. Some work has been done, not on aluminum.

PROF. HIMMEL: No.

PROF. FLINN: No? Which no? Have they not looked or have they not found
any?

PROF. HIMMEL: It is my impression that the photoelectric threshold shifts
to very long wavelengths on deformation. In other words, that you
can get emission at wavelengths which are longer than the threshold
value when you deform.

DR. SMITH: I would sure like to see the reference.

DR. SCOTT: There is some evidence that solid state physics might explain
why you would get emissions at somewhat lower energies, because
people have done optical studies on deformed metals or heavy cold-
worked metals, and they find because of the disruption of the periodic
potential by cold-working, you actually broaden the energy bands in
the material, so some of them are now closer to being free electrons and some are further from being free electrons because you smear things out a lot. This could partially account for the lowering of the work function.

PROF. HIMMEL: Yes.

PROF. FLINN: This again would be more than pure geometric effect.

PROF. HIMMEL: Yes, it would be.

DR. SCOTT: It would be electron structure effect.

PROF. H. TIERSTEN (Rensselaer Polytechnic Institute): Wait a minute, I have a question. In what you did, you took the electrostatic equations of the interior and the exterior of the bond, and there was no surface charge?

DR. KRAUT: That's right—there is not that there isn't any charge, there is locally. The integral of the surface charge is zero.

PROF. TIERSTEN: The integral is zero, but at each point where you matched conditions, the electric displacement of the normal component was continuous?

DR. KRAUT: Right.

PROF. TIERSTEN: And then you took a frequency dependent dielectric constant?

DR. KRAUT: Right.

PROF. TIERSTEN: And you solved that problem?

DR. KRAUT: Right.

PROF. TIERSTEN: And that was because it had a resonance at the plasmon frequency?

DR. KRAUT: Sure.

PROF. TIERSTEN: And from this, you concluded something that related to the photoelectric effect. I am questioning it because of the distinction.
DR. KRAUT: No, what I showed is the plasmon, the so-called plasmon edge, which is a term familiar to people who have been looking at the experimental data for the photoelectric effect. That asymptote, that quantity can be calculated without solving a full set of Maxwell's equations. It can be obtained by solving a set of electrostatic equations.

PROF. TIERSTEN: That's what you showed.

DR. KRAUT: Secondly, when you have an arbitrary surface, you simply can't separate variables. You have to apply an integral equation. And it is a homogeneous integral equation. It has a spectrum of eigenvalues. The lowest eigenvalue corresponds to the plasmon edge, but it is not necessarily 10.6 electron volts anymore. When the curvature varies from point to point on the boundaries, it is a function of the curvature everywhere.

PROF. TIERSTEN: The 10.6, however, is a function of the material?

DR. KRAUT: It also is a function of the material through the plasmon frequency.

PROF. TIERSTEN: There seems to be other conclusions that came from what you said in connection with the whole discussion. That's the reason for the question.

DR. KRAUT: That I introduced or that others introduced?

PROF. TIERSTEN: I don't know who introduced it, but it sort of came up and I was puzzled how the jump was made from what you did to what everybody was saying. That was the reason for the question. I don't know whether you should be the one to explain it.

DR. KRAUT: There is a theory of yield curves. It is called the roughness enhanced plasmon theory, which is due to Endriz, Spicer, Elson, Richie, and a whole number of other people. Okay. Now, that theory says that the plasmon edge, i.e., that the energy that you observe on the yield curve, is a fixed number and has nothing to do with the curvature of the
roughness of the surface. And it is only the coupling to plasmons of different wave numbers that is affected by surface roughness.

PROF. TIERSTEN: You were just saying the jump was made before you ever got into the problem. You are just correcting the problem.

DR. KRAUT: I am just correcting it, right.

DR. DON THOMPSON (Science Center, Rockwell International): If I might try to clarify a little bit, Harry. The idea began with the fact that the photo-enhanced yield increased with the amount of fatigue. Fatigue is known to change the surface roughness through the operation of deformation mechanisms. So, the question that is being asked is, can surface roughening which accompanies fatigue account for some of this increased photon yield? Ed's takeoff then is to explore the effect of surface roughness on the plasmon edge and the yield curves.

PROF. TIERSTEN: On that edge, Okay.

DR. THOMPSON: I would like to make one comment. It is just an intuitive feeling that something may relate in the exo-electron work to something that I think Professor Ebert mentioned. I think it is a very good point. If you talk about residual stress, one is sort of hung out to dry to understand physically what that means, but if you think in terms of residual strain, then there is a physical parameter that is measurable.

Now, the question that comes up here is, do physical, residual strains and their effect upon the electron structure show up in properties such as the exo-electron emission? I think these questions have yet to be answered or even explored, but I think there is a theme that is worthwhile and fruitful to pursue along this line. It is an exploratory game, but as far as NDT is concerned, fatigue is, of course, very important, and I think it is very important to determine the relationships between exo-electrons, fatigue and residual strains that Professor Ebert discussed.
DR. FRANKLIN ALEX (Ogden Air Materiel Area, Hill AFB): I have a question on the residual stress, and it is specifically, is there any particular technique or is there any evidence that has been put out that indicates that there is an increase in residual strain when you embrittle a specimen? The problem I have is that I have been doing some work on hydrogen embrittlement, and if you actually look at the amount of hydrogen that is nominally extracted from an as-received steel specimen, you find it is something like 1000 times that amount which is soluble at room temperature. If you were to go ahead and try to explain the location of the hydrogen, I think it is somewhat evident that it is probably not located interstitially, but it has got to be tied up with some other phenomenon.

The reason I bring this up is that we have some very positive proof that as you inject hydrogen into a specimen, using electrochemical embrittlement, for example, you do increase the dislocation density considerably, and that would suggest there is some sort of a mechanism which is creating either dislocations or creating strain which creates dislocations. The question is, therefore, whether there has been any work done to indicate whether or not the injection of hydrogen into a specimen creates a strain?

PROF. LYNN EBERT (Case Western University): Actually, I am certain that it does, at least on a local scale, and this is where the micro and the macro distribution of strain, residual strain, becomes important. If we cold-work any material, we know we increase the number of dislocations by several orders of magnitude at strains of about 2000 percent. These must be distributed on a nonuniform basis very locally which will produce microstrains and microstresses, tessellated stresses, as these are sometimes called. The macrostrains produce the residual stresses that we worry about. It gets a little bit complicated, but I am pretty certain that is the way it is. We have done a lot of work looking at thin films of these materials, and we can see this. We are very familiar with the role of hydrogen in embrittling materials. I
I am not at all sure that the hydrogen embrittlement is manifested in a degradation of the fatigue resistance. There are two competing factors. One is that if we do, in fact, push hydrogen atoms into the surface such as by flinging them in, we produce a residual compression on the surface. This would enhance fatigue resistance presumably.

We also know that they tend to accumulate in certain preferred sites. These are sites of high coaxial tension and they form pseudo hydrides when their concentration is sufficiently high and, in fact, may form a crack embryo.

So, we have these two competing factors, and it then becomes important to know how much hydrogen we have in the material. I do not personally know of any work that has been done in the fatigue of hydrogen embrittlement materials, but that doesn't mean it hasn't been done, I just know know of it.

I can see that under many conditions, it would actually improve fatigue resistance. It will certainly degrade toughness and a lot of other properties, but it may, in fact, momentarily improve fatigue resistance. We have to do a lot of work on hydrogen embrittlement in our laboratory and we look at it under a lot of different conditions. We have pretty firm ideas of the role of hydrogen, and it only takes five or six parts per million on the average to promote hydrogen embrittlement. This is not a lot more than the equilibrium amounts of iron at room temperature. The trick, of course, is to concentrate it in certain areas. We do this by notching and by producing high coaxial tension stress states so there is a stress-induced diffusion of hydrogen. In this way, we postulate the presence of a pseudo iron hydride. You can show that the dislocation density increases to where you might even say it is a crack embryo, if you look at it hard enough.

Now, this is no answer to your question, but I personally am not in a position to give you a more direct answer. I thought I should attempt to do so because you talked about residual stresses.
DR. ALEX: Well, let me ask you one more question. You said something about the fact that you have stress-induced diffusion. Is there a possibility that what is really happening is that dislocations are acting as traps for hydrogen, and you actually have movement of dislocations and this is, in effect, what is dragging along the hydrogen?

PROF. EBERT: Well, we know if we expand the lattice by coaxial tension, we know it obviously would have to be unbalanced triaxial tension because we can't get any other kind. We can accumulate a lot of hydrogen in these sites. As a matter of fact, it will promote cracks under steady state loading and ambient temperature. The crack ceases to grow, however. It continues to grow only when the hydrogen accumulates behind the crack to a sufficiently high quantity. The point, in fact, is at the edge of a crack, you don't have triaxial tension—you have biaxial tension—and you need the third component, the third tensile component, to expand the lattice sufficiently to make the hydrogen want to fit there. It does, in fact, diffuse to this position, and the crack grows a little bit more, and we can monitor the crack's growth by measuring the resistivity changes as a function of time. This is for a steady state loading in ambient temperature. We believe other interstitials do the same thing, but in order to get the diffusion that we need to promote this stepwise crack growth, we have to raise the temperature somewhat to three or four hundred degrees Fahrenheit. This is the mechanism of hydrogen cracking delayed failure, if you will, or static fatigue. This is well documented in the literature.

DR. THOMPSON: I would just like to make one comment in relation to this question. We made some measurements of the internal friction in niobium as a function of hydrogen concentration, and it was quite evident in following up with standard electron microscopy that there were effects due to the hydrogen which was apparently preferentially precipitating at dislocation cores, that is at in-grown dislocations which had then locally very high concentrations of hydrogen.
This showed up in the internal friction measurements, but more importantly, showed up as punched-out dislocation loops in the material with very large accompanying internal stresses.

PROF. TIERSTEN: I heard no discussion of anybody trying to measure residual stresses ultrasonically in the whole talk this afternoon.

DR. GARDNER: You heard no discussion of people trying to measure residual stresses by a whole host of candidate methods. That just didn't get discussed. I noticed that the Air Force has departed. That's too bad. I notice that the closer you get to fundamental physics, the more likely the Air Force is to evaporate.

Let me make a couple of comments about the other candidate methods.

LIEUTENANT BUCKLEY (Air Force Materials Laboratory, WPAFB): Do you want me here or should I leave?

DR. GARDNER: Stay, stay.

There are, of course, besides those methods that were mentioned and discussed here today, other methods that people have vigorously investigated as candidate approaches to nondestructive measurements, detection, and characterization of residual stresses. One of these, of course, is the ultrasonic technique. There are two basic ultrasonic techniques. One is simply to look and see if velocity itself is strain dependent. The more valuable technique is that of ultrasonic birefringence which is induced by stress where a shear wave of one polarity propagates at a slightly different speed than one which is polarized at right angles to it. The strain sensitivity of the latter technique, however, is not high, but it is entirely feasible. The technique is currently being explored further at the Marshall Space Flight Center in Alabama.

The basic glitch in the ultrasonic birefringence method has to do with texturing. In aluminum, for example, as little as two or three percent preferred grain orientation induces an ultrasonic birefringence equal to that of the yield stress. It is awful hard to get that much texturing by the usual forming operation, so you have to know an awful lot about the effects of preferred grain orientation a priori in order to interpret the results in terms of residual stresses.
PROF. TIERSTEN: What about that question, monitoring loads that are in existence? Is that done?

DR. GARDNER: Yes, it is. There is a NASA-funded project being conducted.

PROF. TIERSTEN: Is it done practically anywhere?

DR. GARDNER: I don't think so. There are other ways to monitor strains, if that is all you want to know. In ferromagnetic materials, one can exploit the strain or stress. I won't get into arguments about what you are measuring, you can exploit the dependence of the magnetic properties on stress or strain. It is an extremely sensitive and well worked out technique based on the Barkausen effect. I will further volunteer that it was developed at Southwest Research Institute. There are some electrochemical techniques in which you attempt to actually infer residual stresses from the changes in surface -- or the voltages between dissimilar materials which are themselves strain dependent. There are other techniques. Is anyone aware of other techniques that have been explored?

DR. THOMPSON: We have explored one other effect that utilizes nonlinear harmonic generation in a propagating ultrasonic wave due either to a dislocation structure or some internal residual stresses.

DR. GARDNER: Yes, you have to have a rather energetic wave propagating through the material before you get these harmonic generations. That is a technique that has been explored.

There is one other I want to mention. In certain favorable cases, nuclear magnetic resonance has been explored as a means of measuring surface residual stresses. Aluminum and Titanium are in this group. George Mascanon at Southwest Research Institute has good evidence on the direct or the conventional method of nuclear magnetic resonance correlated with a theory due to changes. Of course, everyone would like a volumetric method as well as a surface method, and we have entertained
the idea and have made some preliminary exploration of the use of acoustic nuclear resonances as a means of interrogating the volume stresses. There are some other people here who know about acoustic nuclear resonance better than I and they may want to comment on the feasibility for that.

PROF. ROBERT LEISURE (Colorado State University): I know a little about acoustic nuclear resonance. I did some experiments, but I guess I am not really prepared to discuss the measurements of residual stress. After attending this meeting, I will do some thinking about it, but at the moment I really couldn't give you anything.

DR. GARDNER: Well, the main purpose of this meeting is to make people go home and think.

PROF. BERTONI: Could I ask you a question?

DR. GARDNER: Surely.

PROF. BERTONI: On these newer tentative techniques or procedures that you mentioned, how many are designed to describe the stress distribution within the material without destroying? It is a pretty good trick.

DR. GARDNER: None of these methods can tell you very much about volume stresses.

PROF. BERTONI: That's why I asked.

DR. JOHN BARTON (Southwest Research Institute): With the Barkausen method, the Vertol Group, I believe, has shown some correlations that will indicate you can sense somewhat deeper than you can with X-ray diffraction, perhaps. They believe depths of the order of .010 of an inch can be probed.

PROF. BERTONI: I am still concerned about that bar that is an inch and a half in diameter.