

The Discovery of Superfluid ^3He

a lecture by

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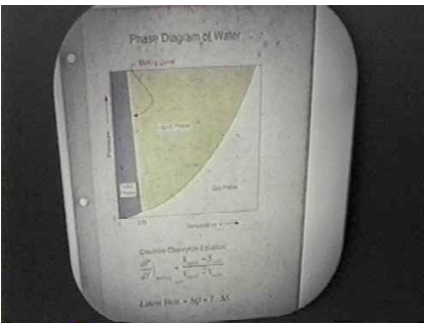
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Timms Centre for the Arts
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Superfluid ^3He was found through a fortuitous accident. The transition was discovered in some pioneering cryogenic experiments and was originally misidentified as the state of nuclear order in solid ^3He . Subsequent NMR experiments, including an early version of magnetic resonance imaging, revealed that liquid ^3He undergoes a surprising pairing transition. The superfluid state is similar to the superconducting state in metals, but with an odd value of the pair angular momentum. The cryogenic technique and early NMR measurements will be described.



The talk I am going to give today is very much a personal account related to the discovery of superfluid ^3He and it lets me illustrate two of my favorite themes in physics and in science. The first is that a very important component of science is the experimental one. Low temperature physics is a field that has some practical applications, and it also has some rather elegant fundamental discoveries (it also has an internal structure that, once one understands the goals, is quite similar to astronomy.) The second, more important in my history of it, is the role of good old-fashioned dumb luck: if you happen to be standing in the right place at the right time with the right apparatus. I am also going to tell a little bit about the implausible steps that I went through, to first become a physicist and become involved in the experiments.

I want to begin with a warm up diagram related to the physics we were attempting when we made our accidental discovery (and this is essentially the only equation by the way, I am going to have in this lecture.) This is the phase diagram of water and it shows



pressure vs. temperature and the regions where there is a gaseous phase, a liquid phase, and, a solid phase, and the important aspect of this phase diagram for practical applications are the lines that divide the various phases. If you could travel in time and sponsor a conference of the leading industrialists of the era

exactly one hundred years ago, and ask what is the most important contribution that physics has made to society in your lifetime, the answer would be this equation right here:

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v},$$

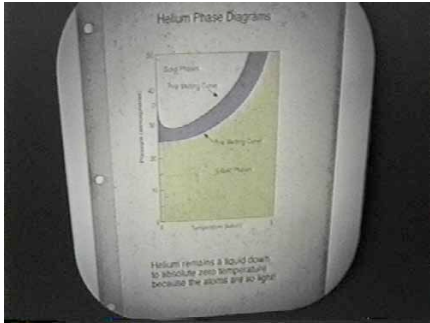
the Clausius-Clapeyron equation. It establishes the ground rules for the energy interchange associated with the transfer of material from one phase to another.

In particular, this portion of the phase diagram up here that divides steam from water was absolutely critical for the industrial revolution, because the machinery for driving all of the manufacturing equipment and transportation were optimized through an understanding of this equation and how to apply it. It's still taught; when I was an undergraduate going to Virginia Tech in the 1950's all of my friends who were in

mechanical and chemical engineering had to take a one semester course called "Steam", and it was devoted entirely to the applications of just this equation to that part of the phase diagram. My friends had these huge diagrams that would cover up a whole wall, that had isochores to analyze it. The professor who taught the course, was rather stern and, as far as students were concerned, a really humorless guy. He was also a preacher in one of the Evangelical Churches in Blacksburg, Virginia. Student folklore said he only had two books in his house: The Holy Bible, and The Steam Tables. All other knowledge was held to be frivolous. So back then that was pretty important.

All right, now, the equation says the slope of this curve anywhere is equal to the ratio of the difference in the entropy between the two phases divided by the molar volume (reciprocal of the density) difference of the two phases. It is not actually a difficult equation to derive if you know the results you are supposed to get! The part that is important for this talk is the line that divides the liquid phase from the solid phase, and in the case of water, and ^3He , and gallium (and one or two other metals, but not very many metals), this line has an unusual property in that the slope is negative. That is, the temperature of the phase change decreases as the pressure increases. There are two reasons why this slope could be negative. If you examine the Clausius-Clapeyron, the numerator could be negative or the denominator could be negative. In the case of water, the density of the solid phase, ice, is less than the density of the liquid phase. Good thing too, because that means that ice floats and lakes freeze from the top instead of the bottom and fish can survive and life could evolve in the way it has. That is also true of gallium. In ^3He the numerator is negative, and there is some interesting physics associated with that. One other thing I might want to mention to make the connection about why the entropy difference is important, is that if we look at this phase diagram at constant temperature, the product of the temperature times the difference in the entropy between the two phases is the latent heat associated with the transition.

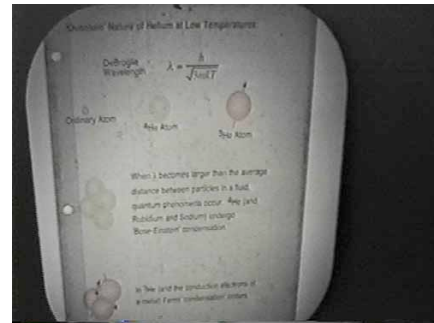
Next I have a cartoon of the phase diagrams of liquid helium. There are two important stable isotopes of helium, ^3He and ^4He . Now helium is an unusual substance because it has very, very weak interatomic forces so that it barely wants to liquefy at all, and it does not form a solid phase without applying extra pressure because of the large amplitude motion of the atoms at low temperatures and the weak interatomic forces. This



is the diagram of pressure vs. temperature for helium. A minimum pressure of at least 25 atmospheres must be applied before ^4He can become a solid phase, and 29 atmospheres before ^3He goes into the solid phase. Then in this region there is a negative-sloped melting curve that is both interesting from the standpoint of

physics and for the technology of cooling. There are very interesting things related to quantum mechanics that happen to both helium isotopes when they are cooled. Why is cooling important? Well, the main thing that happens when a substance is cooled is that thermal energy is removed, so that in these liquid phases of ^3He and ^4He the atoms slow down when the thermal energy is removed, they have less and less momentum. According to the de Broglie relation, when momentum decreases, the wavelength of the particle increases roughly as one over the square root of the mass times the temperature.

In this slide I have sort of a cartoon showing ordinary atoms and ^3He atoms and ^4He atoms at 3 or 4 Kelvin. At these low temperatures, the helium three atom will look larger than the ordinary atom or the ^4He atom. It's got a smaller mass, and this de Broglie quantum mechanical wavelength becomes larger. ^4He



is also much bigger say than sodium or argon because of its small mass relative to the others. There is another important difference between the two, and that is ^3He and ^4He have different statistical laws that come into play when quantum mechanics becomes important at low temperatures. Quantum mechanics become important when this wavelength becomes comparable to the interparticle distances, because the atoms overlap each other; they are aware of each other in a fundamental quantum mechanical sense. In the case of ^4He when that happens the temperature is around 3 Kelvin. The statistical law ^4He obeys with an even number of fundamental particles (electrons, protons, neutrons) is the law called Bose statistics. The interesting thing that happens below there is that once a certain temperature is crossed, it is possible for all of the atoms to drop into one single ground state, called the Bose-Einstein condensate. That is the focus of the interesting work that has been done recently on suspended gases that are cooled to very very low

temperatures using laser cooling and you can have other atoms produce this Bose-Einstein condensate.

In the case of ^3He there is an odd number of fundamental particles, and one has a magnetic moment. It is as a consequence of having an odd number that it obeys a completely different set of statistical rules called Fermi statistics, and that leads to important properties of the system. Another class of materials that are fermions are just electrons, just single particles, and they have to obey Fermi statistics too. Our understanding of the periodic table and why there is a periodicity in the properties of atoms as you add more electrons is really based on the rules of Fermi statistics. No two fermions that are interacting are allowed to have the same energy state. In the case of electrons in a good conductor, or in ^3He , the consequence of that at absolute zero is that no two electrons can have the same state. So the energy of the most energetic of those electrons or ^3He atoms or neutrons in a neutron star is the energy of Avogadro's number of particles in a little chamber. The energy level of the most energetic one is 10^{23} steps above the ground state, and for bosons they are all condensed in the ground state so there is a really profound difference in the properties. As the temperature is turned on from absolute zero, the fermions get excited in a way in numbers proportional to the temperature and that leads to the properties of the "Fermi gas", where heat capacity and entropy are proportional to temperature.

Okay, that is background. Now I want to tell you about the experiments that we were attempting on ^3He . But first I want to take you aside to tell you how I got to this part of the subject. When I started college, if you had told me that I was going to make a career as a physicist and end up as a professor of physics, I would have said you are absolutely crazy. There is no way that is going to happen. I stumbled into a career in physics in kind of a funny way. I started off in engineering and I just didn't have the discipline to make nice lines in mechanical drawing tasks. I wanted to take a more liberal curriculum. I tried chemistry and I did alright in freshman chemistry and freshman physics, but my next level chemistry course was all quantitative analysis. I am colorblind and I couldn't see when phenolphthalein turned from pink to blue and I complained to the professor and he said "tough, if you can't see that you have no business being in chemistry". So then I transferred into physics, because in a way it was the most liberal

curriculum and I was interested in a lot of things. I didn't find it really difficult to get a B average in physics and I wasn't interested in doing much better than that, and I had lots of time to take stuff that really interested me like English literature and history and things like that. I made A's in those (I even got D's in freshman physics courses). I graduated in 1958 and those were the days of conscription in the United States. I took officer training, ROTC, in college, and when I graduated it was an interval of peace, no wars on the horizon, and the Department of Defense had a decrease in their amount of money and they couldn't afford to have all of the officers being trained go on active duty for a full two or three years. I was told that if I would delay going in for one year that I would only have to be on active duty for 6 months and I would only have to be an Ordnance Officer, and I said, "Sold."

So I stayed at Virginia Tech for an additional year and got a Master's Degree so I could learn a little bit about physics. At the end of that time, just before I went into the army, I went on job interviews. The kind of jobs that were available at that time were incredibly boring so my goal when I went into the Army, (and I am going to get to the point in a minute!), my goal was to spend my spare time applying to business schools. My notion was that I would get an MBA and become a captain of industry, eventually the president of General Electric or something like that. So I went into the Army that September and I discovered that I really intensely disliked the officer training courses I was taking. Didn't mind wearing a uniform and qualifying with a rifle and saluting and all of that because if you have armies that is important stuff to do. My personal revelation came about one day when we were taking a course on how to cross reference army ordnance stock numbers with federal stock numbers. I was being trained to run a platoon, in order to fill out the forms you had to know both stock numbers for the parts. I am sure the Army does this with computer assistance now, but in those days you were given these big things that looked like Manhattan phone books and it was a matter of learning how to fill it out. I said certainly there has to be something more creative in life than this type of activity. It occurred to me that it wasn't the fault of the army; in fact, the military trains people to be business managers because that is what an officer is. They probably do it better than anyone else does in the world. So it was at that point that I decided I would take physics more seriously and try to go to a graduate school in physics.

But I was off at Aberdeen proving ground in Maryland, nowhere near any university, and I had burnt all my bridges. I had no really good advice and I had to pick a field and a university. I knew I wouldn't get into a high power place like Cornell so I thought back about things I had found interesting, and the idea of low temperature physics sounded like fun. It didn't have lots of applications so it might not be very, very competitive. And all the really bright people I knew were going into high-energy physics and things like that.

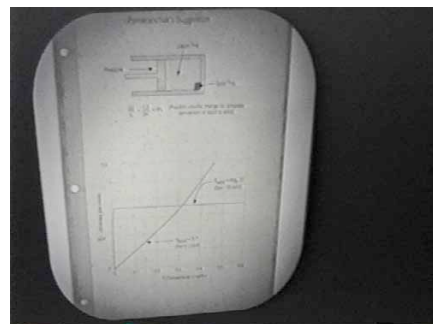
Then I heard of this program at Duke University that had some really interesting things. They had this famous theorist named Fritz London who had done some very important theories about superfluids at low temperature, and an experimental leader named William Fairbank who had done some amazing experiments. So I applied there and got admitted there, and arrived there to discover that Fritz London had been dead for 5 years and Bill Fairbank had gone to Stanford, he had been there for 2 years! I went to work for this delightful man named Horst Meyer. Life is filled with lots of very, very fortunate coincidences and he has turned out to be a great friend and sort of a father figure for me for most of my life. So I started working with Horst and that is how I got my first training in low temperature physics.

The next story related to that is the particular that really led to the accidental discovery of superfluid ^3He . After having been at Duke for about 2 years, the time came to take the oral examination. Duke had a system like lots of American universities at the time where before one is permitted to go the next stage of training, there was an oral examination. A new professor had come to Duke at that time who was on my committee that gave the oral exam, and his name was Henry Fairbank. He was the brother of Bill Fairbank, and he had come from Yale and this was his first year there. Nobody knew what kind of questions he asked, but he brought some of his graduate students with him so I looked up one of them and asked "well, what is Henry Fairbank's favorite question for oral examinations?" He told me the favorite question is about the melting curve of ^3He and the Pomeranchuk effect (which I am going to tell you about in a few minutes). There is another really interesting coincidence, which is that my senior colleague who hired me later at Cornell had been a student at Yale with Henry Fairbank and had probably been asked the same questions about 5 years before I was!

So anyhow I knew how that was his favorite question and so I decided not only to know how to answer that really quickly, but to figure out lots of other stuff. The goal, the dream, of every graduate student is to fill up the entire hour that is allotted with kind of a filibuster. So expecting this question, I prepared an answer that went beyond just the suggestion of Pomeranchuk. The suggestion was really remarkable and I can understand why Henry Fairbank thought that was a very fun question. It was made in 1949 by a Russian theorist who is best known for his work in particle physics. What he said in 1949 was related to a very creative notion about how to cool liquid ^3He . Now what is remarkable about that is in 1949 not many people in the world were aware that there was enough ^3He around to make liquid, much less to do other things. ^3He comes primarily from radioactive decay of tritium. Tritium was being made in reactors in the United States and the Soviet Union for weapons production. It is a central part of the trigger for a hydrogen bomb and in 1949 the hydrogen bomb had not been around very much and the half life of tritium is 12 years so you would think there wouldn't be enough ^3He around to even consider. In fact, the first ^3He was liquefied also in 1949 at Los Alamos but Pomeranchuk did not know about it. For the early experiments they had lots of ^3He it turns out, but they had to use a really tiny quantity of ^3He because neither side wanted the other to know how much ^3He was around because you could track that back to figure out how much tritium was around and then you could estimate the number of hydrogen bombs that existed. So much of my career has been using the waste product of the weapons industry. There are some really fun things that can be done.

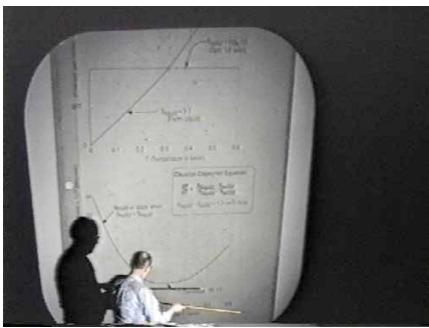
So the notion of Pomeranchuk is based on thermodynamic relations, that Clausius-Clapeyron equation, that if you could take pressurized ^3He at melting pressure, start off with liquid ^3He and squeeze it, decrease the volume in the amount that is required to convert all that liquid into solid without using an entropy change, that this would cool. It is kind of

funny stuff, the solid phase forms on the hot side rather than on the cold side for reasons I will show you in a minute. The reason he said this was going happen was because of the quantum mechanical properties of liquid and solid ^3He . In the case of liquid ^3He the



entropy and heat capacity are like the electrons in a metal and are proportional to the temperature at low temperature. In the case of solid ^3He , when the atoms can't move around and interact in a liquid-like manner you find that the principal disorder is that associated with nuclear magnetic moments. Until the temperature is low enough so that the very, very weak nuclear magnetic interaction between adjacent atoms can dominate the thermal energy, it is completely disordered and the Boltzmann Law states that entropy is going to be equal to k_B times the natural logarithm of the number of states that the system has. ^3He has spin $\frac{1}{2}$ so there are only two states, "this way and that way", so over a very wide temperature range this has the value $\log 2$ divided by R per mole and the liquid is linear in temperature. What Pomeranchuk said was the reason for this cooling is that if we, for instance, pre-cool this material to about $1/10$ of a Kelvin in the liquid phase and perform a reversible pressurization of material (squeeze it without entropy loss), it will track along at constant entropy and end up on the solid entropy diagram at very, very, low temperatures. He estimated that because of the very, very weak interaction between the magnetic moments that this would be 10^{-7} Kelvin. So we can cool from $1/10$ of a Kelvin to 10^{-7} Kelvin, and furthermore we would end up in a state where there is magnetic order in the nuclei. That was the first time there was a notion of having nuclear magnetic order in these kinds of materials.

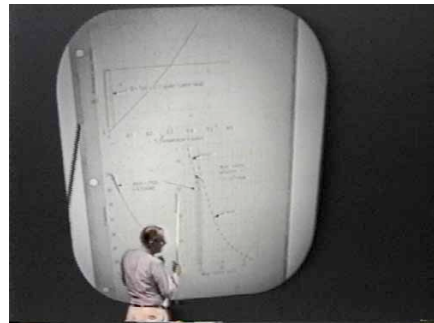
So that is the essence of Pomeranchuk's idea. There is an interesting consequence on the melting curve dividing the liquid and solid phases. I have here again the Clausius-



Clapeyron equation, and note that above 0.32 Kelvin the curves cross each other so the entropy difference is zero, so the slope of the phase boundary between the two is equal to zero and that is what was predicted and measured. As the temperature decreases the melting pressure decreases, and then

below 0.32 the melting pressure increases as the liquid entropy becomes less than the solid entropy. The volume difference per mole is a constant so the notion that you have is of trapped-off ^3He sealed and isolated at low temperatures, change the dimensions of it and the ^3He will by following this pressure vs. temperature curve.

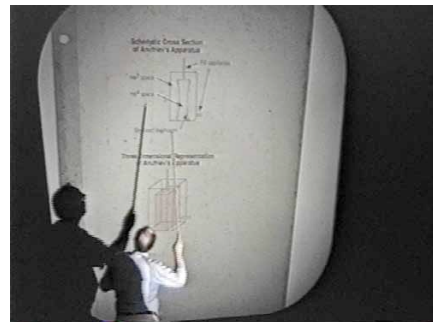
Now the problem with that, which was in the filibuster part of my answer to that oral question, is the efficiency of the process - because lots of things in principle can cool. For example you might have observed illustrated some of the ideas about order and thermodynamics with a rubber band. If you stretch a rubber band, the long skinny molecules try to become ordered, to lie parallel to each other and momentarily there is a little bit of heat. If you let the rubber band equilibrate with room temperature you have the more ordered state, the entropy is decreased. Now if you just relax the rubber band and put it against your lips you will feel that it is cooled off. That is essentially a process that is not drastically different from the one I have described in ^3He . But you would never propose making a refrigerator or air conditioner out of a billion rubber bands that you stretch and relax and blow fan over or something. There are some impractical ideas there. The one that seemed really crazy is the ratio of the amount of heat that could be extracted to the amount of work that is done in the process. The amount of heat that is extracted in this cooling process, for instance if we started at 25 millikelvin, is just equal to the area under this curve, about 0.11 joules per mole. That has to be compared with the amount of work that is done in the process. The diagram that I show here is pressure vs. volume. There is a line associated with the solid-liquid phase boundary, and for the process that began at starting pressure of 33 atmospheres, say, and to decrease the volume by about 5%, the amount of work that is done is about 4.3 joules per mole. Now if that is completely reversible work it doesn't make any difference. There is no heat loss. But if there are some frictional losses or inefficiencies associated with that, if 2% of that squeezing work got lost and went into friction, the process would be to heat rather than cooling off. That certainly seemed the most likely thing to me because in doing some low temperature experiments we had the experience that just a little tiny bump on the side of the Dewar that held the helium and all hell would break loose and you would warm up to high temperatures. So it seemed to me that I could, and I did, argue that it was a really crackpot idea, but it was cute and that is the kind of thing you would expect from a particle theorist.



Well, it turns out that my argument was absolute rubbish and there have been somewhere between 40 and 50 apparatus' designed that cool ^3He by this squeezing and no has ever figured out how to make one that didn't work. They all work. That is essentially because metals lose all of their tendency to have dissipation at low temperatures. If you ring a piece of metal, just strike it and look at how long it rings, the quality factor can be millions into 10 millions.

My whole PhD thesis was related to studying solid ^3He at high temperatures in the paramagnetic phase. We did nuclear magnetic resonance experiments on it and were interested in the amount of motion the ^3He atoms have in the solid phase. The large amplitude zero point motion enters a certain probability that the atoms will trade places, and that actually changes the strength of the magnetic interaction that will lead to magnetic order. In my thesis with Horst Meyer we determined that it was very likely that the temperature at which the solid entropy would drop by large quantities and lead to nuclear magnetic order would be a millikelvin temperature instead of a tenth of a microkelvin. Dave Lee invited me to come to Cornell and see if we could discover this nuclear magnetic ordered phase transition. He said that we were going to try and cool using the Pomeranchuk effect. I was utterly convinced that that was, let's see, the modern euphemism is that that's a "high risk" experiment. In NSF review talk that means "very good", and on a funding scale that means "F". You don't get any money. But he said Cornell is great place, they have lots of other equipment, if this doesn't work we will figure out some brute force method to get there anyway.

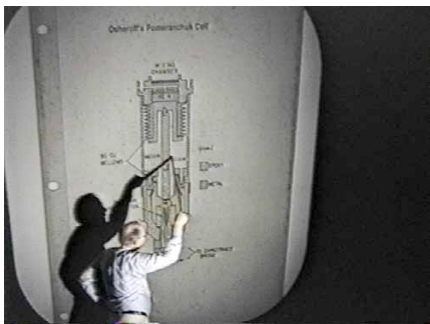
So that is how I went to Cornell. We started in October 1966. I didn't know it then but just before the time that I arrived someone had actually tried this experiment and his name was Yuri Anufriyev at the Kapitza Institute in Moscow. He made a very simple apparatus. It had chambers made in a rectangular parallelepiped geometry. There was an inner chamber to hold 4He and an outer chamber to hold pressurized ^3He . The ^3He was put at the melting pressure and the fill line was sealed off. Then the 4He was forced into the inner chamber and the walls were forced to buckle out so the volume available to the ^3He would be decreased, and the apparatus seemed to



work. The problem that he had, and it is kind of an always-present low temperature physics problem, was measuring the temperature. What he could mainly say was that it did not heat up. He saw it cool down a little bit below his initial temperature. He had carbon resistors as a resistance thermometer on the outside and they didn't warm up. They just cooled a little bit and then they stayed at some apparent temperature for 5 or 6 hours before they started warming up. What that really means is it did cool, but you don't know how cold, it just lost track of where it was.

We had a sequence of graduate students on working on more sophisticated designs at Cornell. There was also the group at UC San Diego of John Wheatley that was doing experiments on this technique, and in Helsinki with Olli Lounasmaa. One of the really neat design ideas that Dave Lee had, because the trick is you have to figure out some way to move the walls associated with the apparatus, was to get a very heavy metal with not very important magnetic properties and attach it to a kind of pulley system that would move it up and down to control the pressure. His idea was to get maybe 4 or 5 kilograms of gold. In those days gold cost \$32.00 an ounce. If we had followed Dave's ideas I am sure it would have worked, and if we had purchased 4 or 5 kilograms of gold we could have funded some rather interesting experiments in the later years after the United States went off the gold standard. We didn't do it that way. We tried bellows and flexible diaphragms.

The third student in the sequence of these experiments was Doug Osheroff. He was actually in on the experimental design from the very first. As a first year graduate student he just sort of walked into the labs and said, "What are you doing?"; and we explained to him the process and he said "The way you want to do that is with bellows," and he started looking in catalogs to find out who made the thinnest bellows. He started



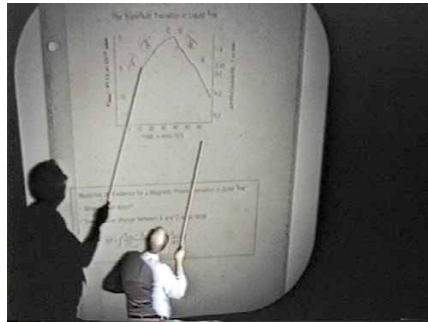
working while he was taking graduate courses and as a teaching assistant on designs of bellows, and over a period of years he designed a particular apparatus. I am not going to talk about a lot of the details but there are two important pieces of this apparatus. There is the lower portion where the walls are made out of epoxy; there is a bellows made out of

beryllium copper, and by just pushing down on the bellows you change the volume that is available for the ^3He . So you go through Pomeranchuk's suggestion for the cooling. The force for pushing the bellows down came from a second chamber that was filled with ^4He . ^4He was admitted into the region, and the pressure was increased. The diameter of the bellows was $4/3$ the other because ^4He solidifies at a lower pressure than ^3He so you had to have some sort of pressure amplifier to take up the difference. In the apparatus' used in the sequence of experiments in 1971 and 1972, all of them contained a gauge for measuring the pressure of the ^3He which was a strain gauge looking at how much the walls move on the ^3He . Our goal was to study this magnetic phase transition in solid ^3He and our technique was to do nuclear magnetic resonance. This apparatus would fit in a thermos bottle, which in low temperature physics work is called a "Dewar" and we had a big iron electromagnet that could roll across the lab on railroad tracks. With 15" pole caps and a 3" gap this was the most expensive and most precious piece of equipment in our laboratory. It must have cost Dave \$8,000 or \$9,000 in 1959. We only had one of those and so we had a number of these Dewars hanging from the ceiling and the railroad track could roll the magnet from one apparatus to another.

Well this apparatus was first built in the fall of 1971. Doug had done some preliminary experiments on an apparatus that had leaked a bunch of times in that fall, and it was his turn to give up the magnet for somebody else. Now I am going to show you what would have happened if he had had access to the magnet in November of 1971. Another researcher in our laboratory had the magnet but Doug had put this together and finally cooled it down and found out it didn't have any leaks. It was around American Thanksgiving, the last week in November of 1971. He said, well, I sure as hell am not going to warm it up because every time that you thermally cycle it there is some chance that the seals between the epoxy and the metal will break open and leak or the basic cryostat will no longer work. So he started doing experiments just to see how the thing would work. What he didn't have was any possibility of looking at the temperature, but the pressure was measured by looking at the strain gauge. The method of measuring temperature was actually looking at the nuclear magnetic resonance signal of platinum, there were some wires that were embedded. Platinum is a paramagnetic material so as it cools to lower and lower temperatures the magnetic resonance signal gets bigger and

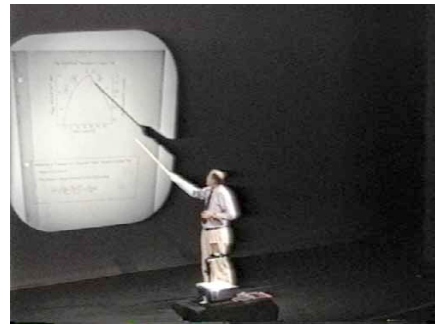
bigger. So in this scheme the important goal to look at was the pressure vs. temperature curve, which was unknown then, and returns some things about the thermodynamics of ^3He . If possible, one cools to the solid magnetic phase transition and see what nature actually does. Well he couldn't measure the NMR signal of the ^3He , or the platinum to tell the temperature, but he could measure the pressure.

So the experiment was just to pressurize the ^4He and watch what happened to the ^3He pressure, and see how far he could drive the bellows before everything would get all crunched up (there might be some heating); and then reverse the process. What Doug noticed in rather careful observations was that a very funny set of things always happened. In a plot here is the change in pressure, relative to the maximum pressure that he observed in the apparatus, vs. time. What he observed was that at a very reproducible pressure the slope of the pressure vs. time curve changed. Now if you recall that there is a relationship between the pressure and the temperature, so that this is the rate of cooling, the cell slows down at a reproducible pressure or temperature each time. It is about a factor of three



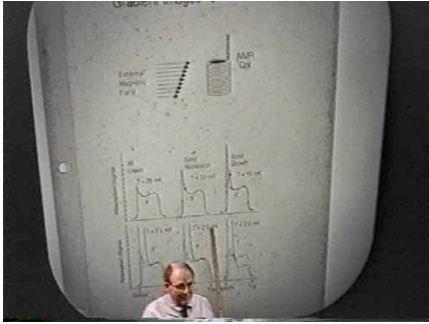
change. The other things that were observed was there always seemed to be an "earthquake" that happened at a different pressure each time; there was a little pressure set-back. And then there was a maximum pressure that was never exceeded no matter what was done. When the pressure was released in the ^4He part of the apparatus, the ^3He pressure would decrease. There was a very reproducible pressure at which the pressure stayed constant or the temperature stayed constant for a very short interval, and then it warmed up and then at exactly the same pressure as before, the slope or the warming rate changed. Well, after some thought the exciting possibility occurred to us that this was happening because there was a change in the heat capacity of the stuff that was in the cell. We thought it was going to be the solid ^3He . If the heat capacity of the material gets larger, as frequently happens in a phase transition, then the rate of warming is going to change if you have a constant heat input or if you are trying to cool at an average kind of rate. We were ecstatic at that possibility. We published a paper, but in the process there were lots of people walking around and looking at this experiment saying, "Oh come on,

this can't be it", when all you've got in there is pressure and time. You don't have any evidence for a phase transition. Beryllium copper must undergo some exotic martensitic phase transition at this particular point. So we built a stainless, Doug built a stainless steel one, replaced it, got exactly the same effect. We became convinced we had seen the magnetic phase change of solid ^3He at this particular point; that was the Holy Grail that we were looking for. We published a paper called "Evidence for a magnetic phase transition in solid ^3He " and this is the place that we said it was happening. In that paper we recognized that there was an embarrassment of riches in this sort of experiment. The first one is, is what is that funny "B" thing that happened every time. The second one is related to our friend Clausius-Clapeyron. You can integrate the equation, and the total amount of pressure change between here and the maximum pressure is 50 millibar, way too large if almost all of the solid entropy is disappearing at this point. So we said, okay, we are just reporting the experimental observation. Nobody has ever seen a nuclear phase transition before; maybe they are different some way or another.



Well I am going to briefly tell you about our next experiments that came after Doug got the magnet back. Bill Tomlinson was the person using the magnet and he went off to Germany and it was Doug's turn again. We decided what we have to do is figure out some way to look inside the cell to see what is going on. You can't literally look like you can through a glass tube and we decided to do experiments we called magnetic gradient imaging. Nowadays it is called magnetic resonance imaging, MRI. This was 1971, 5 years before the patents were taken out on the technique that is used in hospitals all over the country. At the time we did it we knew very well that it was not original to us. In the first NMR in the lab of Purcell, one of the people who invented NMR, his graduate students, just for the hell of it, invented an NMR coil where they looked at 3 different pieces of rubber of different sorts in a magnetic field gradient. They could detect that there was a difference in the magnetic resonance properties of these three materials. It was famous. Bloembergen's thesis, which is the first PhD thesis on NMR, talks about this method.

How does it work? Well the idea is that we have an NMR coil and our ^3He is in this coil and there is a gradient in the magnetic field. So in this example the bottom has a



bigger magnetic field than the top. There is a unique relationship between the Larmor frequency, the frequency of the NMR signal, and the strength of the magnetic field. So we have this system where we have this fixed magnetic field with a gradient and we can sweep the frequency of the detection circuit for

this coil and the top part will come into resonance at a frequency lower than the bottom part. Why we hoped we would be able to see something is once again the quantum mechanical properties of ^3He . Liquid ^3He has the Fermi statistics properties and it has a well known Pauli susceptibility; the size of magnetic signal is not expected to change with temperature. Solid ^3He on the other hand is a paramagnetic. Just like the thermometers we want to use to lower and lower temperature, you have a bigger and bigger signal as a Curie-Weiss law. There is more and more polarization of the nuclei in an applied magnetic field and also the signal will get bigger and bigger as more solid forms. So we did lots and lots of experiments looking at this, studying the size of the solid ^3He signal as we saw these points A and B. It was pretty disappointing, nothing seemed to happen. The signal gets bigger and bigger at low temperatures for solid helium three. But nothing very wonderful seemed to be happening especially since this was supposed to be the world's first nuclear magnetic phase transition.

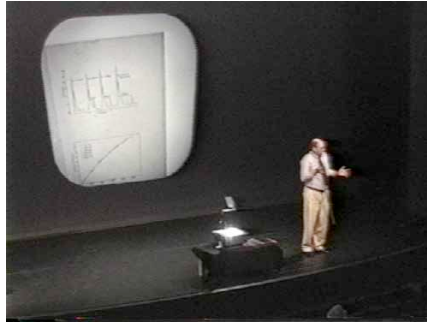
Finally, and this came about through careful analysis of the strip chart recording that Doug was doing this with, it was found that something was happening to the liquid part of the sample. This is an illustration of the type of results that we obtained after we knew what to look for. These traces A through F correspond to frequency sweeps through the resonance at successively lower temperatures as more and more solid has formed as the material is cooled. The first trace is done beginning when there is all liquid. If it were a perfect apparatus with no accidental gradients in the system, this would be just a trapezoid, a flat top. Our real apparatus had screws and O-rings and all kinds of things like that. So there were accidental, inadvertent gradients. So the line looked like this one when it is all liquid. As the apparatus was cooled to lower and lower

temperatures solid ^3He tended to form at the top. At the bottom there was a hot spot intended to seed there and so at 22 millikelvin there is a big signal growing over here because there is some solid ^3He that is formed. As we went to lower and lower temperatures the solid signal got bigger and bigger. By the time we got to the point where the heat capacity change occurs, the solid ^3He signal, the thing that we looked at for a couple of months and hadn't found any enlightenment in studying, that signal would be off the ceiling here on that scale.

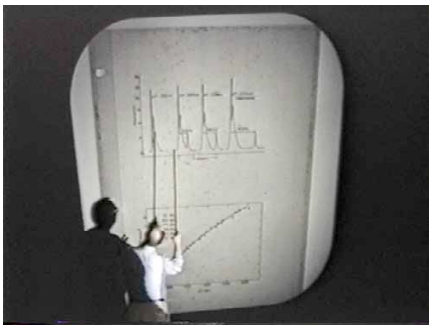
This is now a comparison: the dotted line is the original signal between the A transition and the place called B, in retrospect going back over it. There was a slight change we didn't observe in the position of the shoulder, but what did happen at this point, where this was the little set back in the pressure as we warmed up slightly, is the size of the NMR signal from the ^3He , which is supposed to be independent of temperature no matter what you do all the way down to absolute zero, dropped in half. That was amazing to us, that it just decreased like that. We knew immediately that there was something related to liquid ^3He going on in that chamber at the same time. The A thing must be solid ^3He and B is something happening to liquid ^3He and what can it be? One thing that occurred to us, it could be a magnetic transition like that which occurs in superconductors. In superconductors the electrons pair up and when they form the one spin up, one spin down Cooper pairs that lead to superconductivity, the magnetic signal disappears because they cancel each other. We said that is probably what is happening in this material. The change that is happening here is the transition in ^3He very much like the BCS transition that occurs in electrons in metal. What is funny is we went to lower and lower temperatures, it didn't change at all, it just stayed at roughly half the original size. Now we said "what an exciting life this is!". We've got a magnetic phase change in solid ^3He and a BCS superfluid liquid in ^3He .

I am going to show you one more set of data and what happened when we finally did the experiment that we would have done if the magnet hadn't had to be used by someone else in November. We took the deliberate gradient off the apparatus and decided to look at the nuclear magnetic resonance signal of the ^3He liquid and solid all smooshed together just to see what would happen. It wasn't going to be particularly illuminating because we were getting a signal from all the stuff, it would be kind of

smear of some sort or other. In any case, we were surprised because what happened is this sequence of traces with no deliberate gradient applied, and the little dotted line shows the signal at the starting temperature around 25 millikelvin. Once again if we have a perfect magnet and no accidental gradient of the magnetic field, this would be a spike; very, very narrow. As the system was cooled by compression the signal got bigger and bigger. This is what it looked like in one particular sequence at the pressure very close to the A event, just a little bit lower in pressure, just a little bit warmer. Then shortly after the change in the cooling rate was observed, at a slightly lower temperature, a little shoulder developed on the side of the NMR signal. As we went to lower and lower temperatures, higher and higher pressures the position of the shoulder moved further and further out, and we can see that this was the size and shape and image of the all liquid signal that we had before we started the experiment. Then when we hit the point called B where the pressure suddenly dropped and where in our gradient experiments we knew that the NMR line was still there but was half the original size, this thing just disappeared. Our conclusion then was that this thing just popped back to the original place and had half the size that it had.



This was an incredibly exciting result for us, and it completely shot down our notion that this stuff that we were observing had anything to do with solid ^3He because we see at this A event there is also something quite remarkable happening in liquid ^3He . Why is it remarkable? Well in our very first experiments we saw that this shift was huge, 1000 times bigger than the Knight or the chemical shift that people usually do NMR for. Good thing too, because if it had been a Knight shift or a chemical shift we would never had known it because we had too broad a line to begin with. We found that there was a



universal way to plot the data. If we plotted the square of this frequency, the shift in frequency relative to the initial frequency vs. the pressure change of the point relative to the A transition (which is something proportional to temperature) we got a universal curve.

A very short time after we had these results, Tony Leggett at Sussex University produced a rather remarkable theory with a very non-obvious new set of equations of motion of the spin system that correspond to the notion of Cooper pairs for ^3He that had a very, very different underlying symmetry structure from Cooper pairs in superconductors. What he said was that Cooper pairs in ^3He form with magnetic moments of the pair parallel to each other rather than opposed to each other so they are in a state of $S=1$, and it has three components, plus one, zero, and minus one as the three states that could happen. In this A phase where we see the frequency shift it results from pairs parallel and anti-parallel to the magnetic field, plus ones and minus ones. The parameter is proportional to what is called the BCS energy gap as it is measured in superconductors. At the B phase there is a sudden onset of the $S_z = 0$ critters and the reason the magnetic moment drops is because the ones with spins opposed to each other, that $S_z = 0$ component, have no magnetic moment and disappear from the signal. He made lots of other predictions about the symmetries associated with the wave function and over the following 25 years we have had great fun in our laboratory and lots of other laboratories around the world thinking up fun thesis experiments and phenomena to illustrate. Mark Freeman had a super NMR thesis experiment at Cornell looking at consequences of confinement of this fluid in narrow geometries.

Anyhow that is at least the beginning story of the first few months of superfluid ^3He . Finally, what happened to this solid ^3He that we were looking for? Well my next graduate student was Bill Halperin, and what he finally found was that this limiting pressure, the highest pressure that we could reach is the point where ^3He solid had its magnetic phase change. Doug Osheroff went off to Bell Labs to develop a remarkable experiment where he could look for modes not just in the liquid but in the solid ^3He and then identify the structure of the magnetic ordering in the solids.

That is my introduction to the subject.

