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RUS STUDIES OF CRYPTO-CLATHRATES: PERFECT CRYSTALS WITH THE ELASTIC PROPERTIES OF GLASSES

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ABSTRACT

The low-temperature thermal and elastic properties of glasses are known to be quite different from those of perfect crystals. For example the specific heat in amorphous solids is much larger than the Debye specific heat of crystals, and the thermal conductivity is considerably smaller. Some disordered crystals and quasicrystals were found to have properties very similar to those found in glasses, but remarkably, no amount of disorder introduced into a crystalline solid can produce a thermal conductivity which is lower than that of its amorphous counterpart. Recently, motivated by a search for improved thermoelectric materials, several compounds have been identified that combine the high electron mobilities found in crystals with the low thermal conductivities characteristic of glasses. The common structural feature of these materials is that they contain loosely bound atoms that reside in a large crystalline "cage": these materials are thus "inclusion compounds" or "crypto-clathrates". A particular class of crypto-clathrates is formed by the filled skutterudite antimonides RM_4Sb_{12}, with M a transition metal and R a rare-earth. These filled skutterudites are derived from a regular unfilled skutterudite such as $CoSb_3$, by "filling" the void in this skutterudite structure by a rare-earth. The presence of the rare-earth has a marked effect on the lattice dynamics of these materials. Resonant Ultrasound Spectroscopy measurements were performed as a function of temperature for both the filled and unfilled skutterudites to determine the elastic constants for both structures. These data reveal that an unusual elastic behavior complements the glasslike thermal properties of the La-filled skutterudite: the elastic moduli of the filled compound display a strong temperature-dependence at low temperatures, which indicates the presence of low-energy vibrational modes in addition to the normal acoustic phonons.

TRANSCRIPT

[Transparency 1]

DR. KEPPENS: I would like to talk about the elastic properties of a particular class of materials, crypto-clathrates, particular in the sense that they are perfect crystals but they tend to have very glass-like behavior.

[Transparency 2]

The measurements I am going to show you are a result of a collaboration between various institutes. The materials have been synthesized and characterized at Oak Ridge National Lab. I was very happy to have had the assistance of Albert Migliori and Tim Darling for the RUS measurements and in the past few weeks I have been working at the University of Leuven in collaboration with Professor Laermons.

[Transparency 3]

Before I start off, I would like to briefly remind you of how different glasses and crystals can behave even at very low temperatures. I have made some very schematic representations of some typical properties, like thermal conductivity, which has been plotted, in blue, for crystalline behavior, and in red, for typical glass-like behavior.

Thermal conductivity in a crystal is much higher than in a glass and has a T^3 behavior. A glass shows a linear T-dependence. The velocity change is very different, too. In a crystal there is basically no velocity change at all below a few degrees Kelvin, while in a glass the velocity will first increase according to logarithmic temperature dependence and then reach a maximum before it decreases again.

Finally, the ultrasonic absorption in a crystal is very small and independent of temperature; at low temperatures, in amorphous solids you get a much higher absorption that rises following a cubic temperature dependence and then levels off to a temperature-independent absorption at approximately a few degrees Kelvin.

[Transparency 4]

The measurements I am going to talk about today were motivated by a search for better and/or new thermoelectric materials. Recently a new class of materials has received a lot of attention in research. These materials are called filled skutterudites and they have the basic formula of RM_4X_{12}, where M is a transition metal, X is a pnicogen (phosphorus, arsenic, antimony) and R can be strontium, barium, lanthanum, or any of these listed here.

[Transparency 5]

These materials have a cubic structure, as can be seen in this viewgraph. The metal ions form this cubic sub-lattice. The pnicogens form these rings and the remaining 2 holes in the structure can be occupied by therare earth. If this rare earth is not present, we have just the regular unfilled skutterudite structure.

The special thing about having these rare earth is that these atoms are sitting in an oversized atomic cage and they tend to rattle around their equilibrium position. The rattling has a remarkable effect on the thermal conductivity, specifically on the contribution of the lattice to the thermal conductivity.

[Transparency 6]

In this viewgraph, I have plotted the thermal conductivity for just a regular, unfilled, skutterudite and I have plotted it for 2 of the filled skutterudites and you see there is a dramatic increase of the thermal conductivity over the whole temperature range.

The nice thing about this decrease is that it happens without deteriorating the electronic properties too much. In other words, these materials are an excellent example of what is called an electron-crystal-phonon glass. This means that the phonon properties are very glass-like, while the electronic properties are just as expected for a perfect crystal, and this property makes these materials a very interesting class of thermoelectric materials.

[Transparency 7]

Very recently another class of materials has been discovered that behaves almost the same. These materials are the clathrates, with the formula X_8E_{46}, where E is like silicon germanium or tin, could also be aluminum or gallium, and X is sodium, potassium, rubidium, cesium, strontium, or barium.

These clathrates are built up by 20- or 24-fold polyhedra, formed by the E elements, and the X atoms are sitting, inside these cages formed by the E atoms. Just as in the skutterudites, these atoms have lots of space and rattle around their equilibrium position, with a drastic effect on the thermal conductivity, as seen in measurements taken by George Nolas and his co-workers.

[Transparency 8]

The upper panel shows the lattice contribution to the thermal conductivity as a function of temperature for 2 of those clathrates, the red curve and the green curve, and for comparison you

see the curve for amorphous germanium. The thermal conductivity has about the same order of magnitude in the crystals compared to the amorphous materials.

It is not just the order of magnitude that is glass-like; it is the whole temperature dependence. As you see in this viewgraph, the red markers represent the data for the $Sr_8Ga_{16}Ge_{30}$ clathrate. The blue markers are the data for amphorous SiO_2 and you see those two behave very alike, although one is a crystal and the other one is a glass.

[Transparency 9]

I am going to focus on the elastic properties of these materials. I was able to get RUS measurements on both filled and unfilled skutterudite samples. For the unfilled I used a $CoSb_3$ sample; I had a lanthanum-filled skutterudite to compare the specimens with each other. Both were polycrystalline, so we just had to get C_{11} and C_{44}. At Los Alamos I was able to do these measurements as a function of temperature between 5 and 300 K.

In the past few weeks I was able to do some pulse-echo measurements, not on the skutterudites but on the clathrates. I had a $Sr_8Ga_{16}Ge_{30}$ single-crystal specimen and I was able to take data at very low temperatures, between 0.4 K up to 30° K.

[Transparency 10]

Let's start off with the RUS results for the regular skutterudite $CoSb_3$. I have plotted the C_{11} and the C_{44} as a function of temperature. The red markers are the data we took and the blue solid line is a fit to what is called the Varshni function, which is a function that has been proposed by Varshni after he observed that basically all normal-behaving solids have a very typical elastic behavior that can be described by this one formula that contains two fit parameters s and t. You see this $CoSb_3$ is one of those normal-behaving solids as it can be well described with this Varshni function.

[Transparency 11]

In comparison to that, if you look at the lanthanum-filled skutterudite, I have plotted the C_{44}, here in blue for the filled sample and, just for comparison, in red, the data I got on the unfilled $CoSb_3$, you see that at low temperatures there is quite some difference in these data. The $CoSb_3$ just levels off and flattens at low temperature while there is this remarkable temperature dependence in the filled skutterudites. It is impossible to just describe this with this Varshni function, so something is happening in this filled skutterudite and, since it is not happening in

$CoSb_3$, we assume it has to do with the presence of this filling atom that is rattling in this skutterudite structure.

Trying to figure out what is going on here I tried to fit the data, assuming that this rattling atom causes the presence of one or maybe more harmonic oscillators in this material, but just assuming harmonic oscillators does not give this temperature dependency observed.

In a second attempt I just reduced the harmonic oscillator to a simple 2-level system.

[Transparency 12]

To get the contribution of a 2-level system to the elastic constants, all you need to do is take the second derivative of the free energy to strain, which is straight forward as long as you assume that the spacing between the 2 levels has only a linear strain dependence.

If you do that and you calculate the second derivative and plot the data, you'll find that the one 2-level system still does not do the job, but taking 2 of them, one with spacing of 50 K, one with spacing of 200 K, I got a pretty good description of the experimental data, as you can see in this viewgraph.

[Transparency 13]

If I take a background, which I estimated from the Varshni behavior of the unfilled $CoSb_3$ and I take 2 2-level systems, one with 50 K, one with 200 K spacing, it just describes these data quite nicely, not just the C_{44}, but also the longitudinal modes, C_{11}. It can be described just taking the same 2-level systems with spacing of 50 K and spacing of 200 K.

[Transparency 14]

In the meantime we have also done some specific heat measurements and neutron-scattering data and all measurements tell us the same. There are 2 2-level systems present in these lanthanum-filled skutterudites that are not present in the unfilled ones, so they have to do with these lanthanum atoms rattling around in this structure.

It would be nice to see if other materials have this same behavior and to do RUS on other filled skutterudites, or on those germanium clathrates but, unfortunately, at Leuven I do not have RUS facilities available. However, I was able to do ultrasonic absorption measurements on the germanium samples I got from Oak Ridge.

[Transparency 15]

I have brought my results, which had ultrasonic absorption data as a function of temperature down to 0.4 K. I could take data at several frequencies, so I have brought data that I took at 250 MHz (in blue) and data I got at 155 MHz (in red).

You see that at low temperatures there is basically no frequency dependence in the absorption, which rises with temperature, almost following a cubic law in temperature, leveling off to show a maximum at high temperatures.

If you remember from my first viewgraph, this is not a crystalline behavior at all, because in a crystal you would expect no temperature dependence at all in the absorption until 20 or 30° K, so this behavior, although we have a single-crystal sample, is not crystalline at all.

[Transparency 16]

On this viewgraph I have plotted ultrasonic absorption taken on germanium oxide, which is a typical example of a glass. For comparison I plotted again the data I took on this clathrate sample. As you can see, both behave very similarly, there is no frequency dependence at lowest temperatures and the absorption levels off, in the case of the germanium oxide, to a plateau-like temperature-independent absorption around a few degrees Kelvin, which is proportional to the frequency.

Both materials behave the same, although you should remember that one is a perfect crystal and the other is a glass. The only remark to make is that the clathrate does not really have a plateau around a few K, it is more like a maximum.

[Transparency 17]

I am not going to bore you too much with the model to explain glass-like behavior but I just want to mention that all glass-like properties, thermal conductivity, specific heat, absorption, velocity, they all can be explained quite well by a phenomenological model that is called the tunneling model. This model assumes that in a glass there are atoms or groups of atoms that have 2 equilibrium positions, so they usually present it as a particle that can move in a double well, 2 wells separated by distance d, having a symmetry Δ and an energy overlap Δ_0.

So transitions from one level to the other can occur at the lowest temperature through tunneling through this barrier. This model can explain glass-like behavior quite well, assuming that those parameters, Δ and Δ_0, have a very broad and uniform distribution.

The basic assumption of this model is needed to explain the temperature-independent behavior observed in all glasses around a few degrees Kelvin. The fact that we do not really

have this temperature independence in $Sr_8Ga_{16}Ge_{30}$ but some kind of a maximum may just mean that this broad distribution that is typical for glasses is not really present in our germanium clathrates, but could be limited to some particular values.

Anyhow, I think these data indicate that this germanium clathrate definitely has very glass-like behavior and has some tunneling states in it.

[Transparency 18]

This brings me to the conclusions. I tried to explain that these filled skutterudites have at least 2 local modes, and that the germanium clathrates are probably full of tunneling states. These two materials are 2 examples of perfect crystals that have very glass-like behavior as far as their elastic properties are concerned.

For future work I think it is obvious what has to be done. I would like to do some RUS measurements on this clathrate I just showed you and get some attenuation measurements on a crystalline skutterudite and compare to see if both samples behave similarly.

Thank you.

DR. MARSTON: What properties in a skutterudite material, the filled ones, extend all the way to room temperature?

DR. KEPPENS: Thermal conductivity definitely is much lower over the whole temperature range. I am not sure about the temperature dependence. For the clathrates I do not have any data up to room temperature. The data I showed you for the skutterudites were taken all the way up to room temperature and it drops just tremendously over the whole range.

DR. LEVY: I was slightly confused with one of those curves. It seems as if by adding the impurity, or whatever, the additional interstitial atom, you decreased your effective elastic constants? The background was higher.

DR. KEPPENS: Especially the effect of the 2 2-level systems brings the elastic constants down. If we had just the Varshni it would be higher than if you add those 2 oscillators which have a negative contribution.

DR. LEVY: Could you show me the original data, the ones where you were trying to explain this?

DR. KEPPENS: This one, before I did the fits.

DR. LEVY: Yes, that one. Okay, now it makes sense. Why is it softer in addition to the fact that the theory tells you it is softer? Do you have any physical idea in addition to the

theoretical explanation? I usually think if I add something it would make it stiffer and here it makes it softer.

DR. KEPPENS: Because the atom is so loosely bound, and it is bouncing around in its cage.

Thank you.