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Condensed matter physics in the 21st century: The legacy of Jacques Friedel

How the Friedel oscillations entered the physics of metallic alloys

*Comment les oscillations de Friedel firent leur entrée dans la physique des alliages métalliques*Émile Daniel¹

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ABSTRACT

Considered first as a by-product of his theory of screening, the Friedel oscillations, when compared with certain NMR experiments, turned out to be a major component of the physics of metallic alloys.

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R É S U M É

Considérées d'abord comme un sous-produit de sa théorie de l'écran, les oscillations de Friedel, confrontées à des expériences de RMN, se révélèrent une composante majeure de la physique des alliages métalliques.

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1. The theory of screening

According to classical physics, no uncompensated electric charge can exist inside a metal. This means, at the atomic scale, that if an atom with a different valence is substituted for an atom of a pure metal, the extra valence electrons introduced in the conduction band pile up around the foreign ion in order to screen its excess (positive or negative) ionic charge over a microscopic distance. From a quantum mechanical point of view, the screened foreign ion appears as a scattering center for metal conduction electrons. An electron passing far from this center, and therefore with a high angular momentum for a given velocity, will be only weakly disturbed by the impurity while it would be strongly scattered if coming very close to it, that is with a small angular momentum. In a model where the metal conduction electrons are taken as a free electron gas and the impurity is represented by a short-range scattering potential with spherical symmetry, it is natural to analyze the perturbed conduction electrons wave functions in terms of spherical partial waves of well-defined orbital momentum. As the amplitude of a partial wave of momentum l decreases as r^l at a small distance r towards its center, only those waves with a small orbital momentum, i.e. mostly of type s , p or d , will be strongly modified, in agreement with the semi-classical picture given above. At distances larger than the range of potential, the modification appears through a phase

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shift in each partial wave. In 1952, J. Friedel demonstrated his famous sum-rule giving the total screening charge through the sum of phase shifts of the conduction electrons at the Fermi level, weighted with their orbital degeneracy. This sum-rule is very powerful because, in practice, it requires the calculation of only a few phase shifts and these need be found only for electrons at the Fermi level.

A plane wave is a unique superposition of partial waves. When their phases are modified, the uniform density of the plane wave is lost. As a result, an oscillating variation of the conduction electrons density appears in the metal, whose amplitude decreases at large distances due to the lesser relative weight of low momentum partial waves. From the very mechanism of their formation, it is obvious that the occurrence of oscillations in the electronic density around an impurity in a metallic material is a quite general effect of screening and is in no way limited to the simple model in which Friedel demonstrated them. Were these oscillations of any importance in the physics of metallic alloys? Nobody knew at that time and Friedel himself did not believe it at first, as he said in his lecture at the Varenna summer school of 1957. For an impurity almost completely screened in its atomic cell, no important perturbation was expected outside, in the bulk of the metal.

2. Experimental facts to be explained

In the course of the 1957–1958 winter, Friedel sent A. Blandin and me to a conference held at Harwell, in England, presumably on the physics of metals, of which I do not remember anything except how difficult it is to get a second piece of bread at a British lunch. While there, we visited L.E. Drain who was doing measurements of the Knight shift in dilute AgCd alloys. The Knight shift is the difference in NMR frequency for a nucleus in a metal with respect to its value in a non-conducting material. It arises from the Pauli paramagnetism of the conduction electrons, which are polarized at the Fermi level by the applied magnetic field. Through their contact interaction with the nucleus, they usually increase the resonance frequency. Drain was perplexed. If the screening of the solute Cd atoms in Ag were perfect, as Friedel had suggested, no change should be seen in the resonance frequency of the surrounding Ag nuclei. However, not only the Ag resonance frequency diminished proportionally to the concentration of Cd, but even a small quantity of Cd atoms produced a very large broadening of the resonance line. Moreover, the same thing happened to the Cd resonance line and the relative change in Knight shift of Cd decreased linearly with the same slope as that of Ag. Drain kindly gave me a sheet of paper on which he had plotted his results. On my return to Paris I showed it to Friedel who became as puzzled as Drain was. Then the paper remained a few months in a drawer of my desk.

The next spring, a conference of the “Société française de physique” was held at the “Cité universitaire” in Paris, which I attended together with Friedel. Meanwhile, he had received preliminary results from T. J. Rowland who was doing in the USA the same kind of studies as Drain in Harwell. Among other things, Rowland had made Knight shift measurements on a series of dilute alloys of Ag with impurities of increasing valence: Cd, In, Sn, Sb. He had obtained results similar to Drain’s, with a magnitude increasing with the valence of the solute atom: roughly, the higher the valence, the steeper the slope of the relative Knight shift versus concentration and the broader the line width. At the conference, we met N. Bloembergen with whom Friedel had a long conversation about this problem. Back at the “École des mines”, where he had his office, a small room opening on the Luxembourg garden and that he shared with us, he told me (in French): “You should try to see if the oscillations could account for Drain’s results (and Rowland’s as well)!”

3. The Friedel oscillations give the answer

At that time, we had no electronic computers. We used to do our numerical calculations by hand or with a slide rule and existing numerical tables. It was quite impossible to make any self-consistent calculation of the electronic structure of an alloy. We had to look for a simple but reasonable model. We thought that it would not be too bad to take for the screened impurity a spherical potential well occupying its atomic cell, its depth being calculated so as to satisfy the Friedel sum-rule. This potential would act only on the plane wave part of the Bloch wave functions of Ag as we neglected any change in their periodic part from the bottom of the band up to the Fermi level. I had to compute the phase shifts and the amplitudes of the partial waves at the nuclear sites for each layer of Ag atoms surrounding the impurity.

Because of the oscillations, the electronic density at the Ag nuclei changed from layer to layer, but all the nuclei of a given shell experienced the same electron density, and therefore had their own Knight shift. I found that for high valence impurities such as In or Sb, the relative changes of Knight shift on the first or second neighbors shell could amount to five percent so that with sufficiently fine resolution they should appear as satellite lines in the Ag NMR spectrum. This was not yet the case although Rowland detected such satellites some time later in some of his alloys. To compute the mean value of the Ag resonance frequency, I assumed perfect disorder of the solute atoms. Neglecting multiple scattering for dilute alloys, I obtained a relative diminution of the Knight shift linear in the concentration of solute atoms, with slopes in very good agreement with Rowland’s results, especially for the high valence solutes In, Sn and Sb in spite of the crudeness of our model. (Many years later, one of my former thesis students, N. Stefanou, then at Jülich in Germany where he had access to a big computer, made a more realistic calculation using the atomic sphere approximation. He did not obtain results significantly different from mine apart from the screening charge, which he found slightly more spread out.)

Moreover, as a scattered wave perturbs a given site in the same way whether it is occupied by an Ag or a Cd atom, one finds the same slope for both their relative Knight shifts, in agreement with Drain’s measurements. Of course, I could not

give a shape to the Ag resonance lines, so I made just a second moment estimate of their width that gave good orders of magnitude.

To conclude, it was then clear to us that the Friedel oscillations could give rise to rather long range effects in metallic materials such as, for instance, chemical interactions between solute atoms or spin glasses in the case of magnetic impurities.

Details on the calculations and experimental results can be found in references [1–5].

References

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