Magnetism

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The research work of P.-G. de Gennes started with a thesis in the nuclear research center of Saclay, where he analysed the neutron scattering by magnetic fluctuations in nickel. He extended a similar treatment to the electrical resistivity of rare earth metals and then explained the magnetic coupling of their 4f shells as due to a double scattering of magnetic origin. He had meanwhile other interests, notably in resonance effects in magnetic materials and even on percolation in alloys. I explain what was new and influential in his *magnetic* activities and what role they played in his early contacts with C. Kittel in Berkeley and H. Casimir in Eindhoven, as well as for his recruitment in the new science faculty of Orsay, where he would soon develop an interest in superconductivity that he caught in Berkeley. I stress the importance played by such early contacts on his future research activities.

1. Introduction

I first met de Gennes when talking with Abragam on the Saclay campus. It must have been in 1955, when I became a consultant with Grison in the metallurgy department in Saclay. De Gennes had recently arrived from the Ecole Normale Supérieure of Paris and from a short experimental stay in Aigrain's then burgeoning laboratory on semiconductors. I had met Abragam in Oxford, when visiting from Bristol with Mott; and we both were recently back from our stays in foreign countries and our British PhD's. De Gennes gave me a deep bow and made a nice comment on my 1952 paper on impurities in metals. The tone of his voice implied that he was in a hurry to be able to publish something too and reach what he saw as our exalted stations in life. In fact, Abragam had just complained to me how hard it was to start an experimental lab in Saclay; and I had only a small bureau in the Paris School of Mines, just starting to teach, with no prospect of any lab room. For the three of us, "born too late in a world too old" seemed to apply, although we had in fact good cards to play.

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2. Magnetic Neutron Scattering

De Gennes was then preparing a “thèse d’Etat” in Saclay, under the busy but kind guidance of Yvon, a known specialist of correlations in liquids and scientific director of the Saclay establishment. De Gennes was meant to analyse theoretically the magnetic neutron scattering of nickel near the Curie temperature. The experiments were carried out by Magda Ericson, a young physicist coming out of the Ecole Normale Supérieure de Sèvres herself. France had at that time in Saclay one of the few nuclear reactors dedicated to fundamental research in condensed matter physics; and I still remember the envious looks of Lévy-Bertaut, the crystallographer from Grenoble, sent on an exploratory visit to Saclay by Néel, who had just obtained from the French authorities the money to build a nuclear reactor in Grenoble for his own use on magnetism.

In Saclay, the whole group was headed by Herpin, a fairly young university trained physicist, who was then to write on magnetism a general book that Néel had dreamt to write all through the war, but was always distracted by new ideas when starting a new chapter![1] Herpin was helped by some confirmed experimentalists in crystallography, such as Mériel and Cribier, and by a group of younger physicists, theoricians as well as experimentalists. They worked on the structure of magnetic crystals and their thermal excitations, but also on correlations in liquids for Yvon and phonon spectra in crystals, following previous X-rays works by Laval and Curien. Of this group, Villain would make himself known early by his study of helical magnetism in crystals and Jacrot would develop later studies of biological materials in the Laue Langevin laboratory in Grenoble. Some of these young people would stay in Saclay and keep active contacts with de Gennes, especially Sarma and Saint James in the theory of superconductors and Janninck and Joanny in the neutron scattering of polymers.[2]

One must remember that, at the time of de Gennes’ thesis, this group followed Néel in describing the magnetic properties of transitional metals in terms of a phenomenological model of atomic magnetic moments of given strength, ordered at low temperatures and progressively disordered with increasing temperature. This model had been introduced by Weiss; and his group in Strasbourg (mostly in Sadron’s thesis) had measured and analysed in this way the magnetic properties of the transitional 3d metals and of many of their alloys. Weiss had assumed that, in ferromagnetic order, each atomic moment was coupled with all the others, by a coupling of uniform strength, independent of distance. But already before the war, Néel had pointed out that, if only neighbouring atomic moments were coupled, a better description of magnetic fluctuations was obtained in the paramagnetic range above the Curie temperature; also, assuming for some metals or compounds a tendency to antiparallel coupling at short range, one would produce an antiferromagnetic structure which would explain the properties of metals such as Mn or Cr and of their oxides. As stressed in the first International Conference on Magnetism, held in Strasbourg in 1939,[3] another group of physicists, led by Slater and Mott, considered transitional metals as conductors,

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with delocalized electrons, occupying partly a narrow energy band of mostly 3d character. Their local exchange and correlation interactions within each atomic site could lead at low temperature to a magnetic instability and different populations of the two halves of the 3d band with opposite spin directions. In the ferromagnetic case, the moment per atom could be a fractional number of Bohr magnetons, as was experimentally observed, despite a negligible $l\ s$ coupling. In 1939, the only analysis of the thermal excitations of such a delocalized scheme was due to Stoner; using a free electron model, with no characteristic length of atomic size, it was unable to explain the paramagnetic atomic disorder observed by the experimentalists. Also no model explained why antiferromagnetism should be observed for nearly half filled 3d bands; and indeed the whole concept of antiferromagnetism was hotly disputed by many.

It is in this framework that the new neutron scattering technique was developed after the war. The low temperature antiferromagnetic structures of metals and oxides were first observed by Shull in Brookhaven; and Herpin's group was checking the other predictions made by Néel, that atomic moment of strength independent of temperature were coupled by only short range interactions.

To analyse the experimental data, de Gennes first showed that inelastic scatterings were only important at low temperatures and that a static approximation of the spin disordered was dominant near T_c and above.[4] In that range he used a second order and molecular field treatment due to Van Hove. Starting from nearest neighbours interactions, this described the long range correlations induced around each magnetic moment, both in the paramagnetic and in the ferromagnetic ranges. It was a definite improvement on previous statistical analyses that restricted correlations effects to nearest neighbours, as used by Néel. Van Hove's procedure was known not to converge in the immediate neighbourhood of the Curie point, a defect which would be improved only later by Wilson's scaling procedure. The Van Hove approximation was however good enough on a large range of temperatures above and below T_c to check Néel's model.[5] The agreement with Ericson's measurements[6] was good enough for them both to present their theses in quick succession. De Gennes extended his analysis to antiferromagnetics above the Néel temperature.[7] He also considered the neutron scattering by liquids;[8] despite Yvon's theoretical contributions to the field, one would have however to wait for Verlet's later computational model in Orsay to have a clear idea of the dynamic short range order in liquids.

3. Rare Earth Metals

During the same period, it happened somewhat by chance that de Gennes attacked the electronic origin of the magnetic couplings of atomic moments in metals. This development occurred for rare earth metals, where the scattering of the delocalized 3d electrons by the magnetic 4f shells is in a way similar to that of the neutrons by the atomic moments in Néel's model of transitional metals. This work played a significant role in de Gennes's carrier. The later works done in Orsay in the 60's on the magnetism of transitional metals and alloys were also inspired by that study. This is why we treat in some details this work, which introduced de Gennes into the electronic structure of metals.

3.1. *Electronic resistivity of rare earth metals*

During my weekly visits to Saclay in the late 50's, I was encouraged by Grison to find my way out of the metallurgy department. I had many friends on the Saclay campus, who had studied with me at Ecole Polytechnique. But I soon focalized on Herpin's group and its various activities on magnetism. I often had lunch with that group, sometimes in one of the still very simple village restaurants of Villiers-le-Bâcle or Gif-sur-Yvette, occasions for animated discussions on physics and politics, especially with the younger members of the group.

De Gennes kept rather more to himself, but I made a point to go and chat with him for a time nearly every week. He had a wide interest in the physics of solid state, interacting not only with Yvon and Herpin's group but with Abragam on magnetic resonance; and, as I discovered recently, he gave lectures at his Ecole Normale Supérieure on fermion gases, in a first version of a course on modern physics launched at the time by Brossel and Cohen-Tannoudji. One of his more exotic interests was the percolation problem in crystalline solid solutions, for which he had induced the manager of the large computer used in Saclay to work out the limits of nearest neighbours hopping conduction for disordered solutions in various lattices, as described later in his book.[9]

I told him of course of my interests of the time. One was on the concept of virtual bound levels, obtained by a resonant mixing of atomic bound states with a band continuum of delocalized states, of similar energies. I had learnt of such states in Bristol, in lectures in nuclear physics given by a member of Powell's group of cosmic rays. I had also found them in Mott and Massey's book on atomic collisions, and had applied the concept to explain the strong scattering properties of d states of transitional impurities in nearly free electrons metals such as Cu or Al. I was then exploring other possible experimental examples and thought of the rare earth metals, with partly filled and magnetic 4f shells interacting with delocalized 3d electrons. If the 4f shells had energies near enough to the 3d band to mix together, one would rather easily predict the way their strong scattering should vary though the 4f series. Trombe, the French specialist on rare earths then working in nearby Meudon, showed me however that the measured resistivities were much too small for such a scheme, except perhaps for borderline cases such as Ce and Yb. This was disappointing to me. But if 4f shells were really localized, they should simply scatter the 3d electrons by a weak exchange term, much as neutrons were scattered by magnetic atomic moment in transitional metals. One knew that these 4f shells were magnetically coupled at low temperatures and disordered at high temperatures: there was a strong analogy between the two cases.

De Gennes did not say much. But ten days later, I met him at the entrance of the Luxembourg garden, on the Boulevard Saint Michel. He was bringing to my bureau, in the neighbouring School of Mines, the paper that is reproduced here unchanged (Fig. 1),[10] for which he insisted that I would join my name!

This is, I think, the first paper of substance completely written by him alone. As for his neutron work, de Gennes assumes the delocalized 3d electrons to be free. He concentrates his efforts on the resistivity due to magnetic scattering near the ordering temperature T_c. He shows that, in that range, the scattering is essentially elastic and can be treated in the Hartree Fock approximation. The break at T_c of the thermal variation of resistivity can be explained in a simple Weiss molecular field, leading to a constant term above T_c. The effects of magnetic correlations, treated in the Van Hove technique for short range interactions, lead to weak deviations from the Weiss model, except for a peak of resistivity at T_c. This is however strong only if half the Fermi wave length is larger than the interatomic distance. Such a condition can be fulfilled for neutrons in magnetic crystals, leading to a "critical opalescence" effect.[11] But it is not fulfilled for electrons in metals, especially for the essentially trivalent rare earth metals.

The final discussion shows an attention to details. Thus the coupling with phonons does not change results much. The physics of low temperature spin waves should require a more refined model. The assumption of free electrons for 3d band is oversimplified both because of their 3d character and, for ferromagnetic couplings below T_c, because of the small decoupling of the two half 3d bands opposite spin. It is finally mentioned that a similar analysis should hold for magnetic transitional alloys such as AuMn or Au_3Mn, with similar variation of resistivity with temperature but especially large magnetic effects due to the resonance scattering of the 3d shells of Mn, as indeed observed.

This early paper clearly shows de Gennes' special gift to concentrate on simplified sketches where only the essential features are kept, while keeping in mind the conditions of validity of such caricatures: it is no surprise that he was a fine drawer! This paper shows also the ease with which he could transfer a certain type of analysis from one field to another, a technique that he would use repeatedly in the future. As the note added in proof stresses, we did not know that Kasuya had similar ideas at the time.

3.2. *Magnetic couplings of rare earth metals*

Shortly after this work, de Gennes published a short note on the properties of rare earths metals[12] that he would develop in the context of a magnetism conference held in Strasbourg by the Société Française de Physique.[13] This talk extends the previous work on resistivity to the indirect magnetic coupling of the 4f shells, analyzed as due to a second order scattering effect of the 3d electrons on two different shells. It was in fact the fairly direct application of an approach then recently developed under Kittel's impulsion to describe the indirect magnetic coupling of two nuclei via their scattering with a gas of delocalized electrons, the now called RKKY interaction.[14]

The predicted variation of stability of the magnetic phase with the filling of the 4f shells in the rare earths series was in striking agreement with experiment, only involving an exchange scattering term deduced from the measured resistivity. Of course the analysis, based on a rough free electron model of the 3d band and on a weak coupling scheme, was hotly disputed by some rigorists. It will be improved by looking at various possible forms of magnetically coupled phases, starting with de Gennes himself,[15] and later by Rocher and Coqblin in their thesis works in Orsay as well as by Mackintosh in Copenhagen for crystal field corrections. This model for rare earths will soon inspire my own admittedly qualitative description of the magnetic couplings in transitional metals: here, weak magnetic moments, developed on different atoms by their atomic exchange interactions, interact, as in the RKKY interactions, via the spin modulations that each one produces at long range in the 3d electron gas. As those modulations have a wave length related to the average Fermi wave length, this explains

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the change from ferro to antiferromagnetism when, in Mn and Cr, the 3d band becomes nearly half filled.[16] And, as pointed out by Lederer in his thesis, such magnetic moments should survive above T_c or T_N if, as likely, their local exchange stabilizing energy, computed in a tight binding approximation, is stronger than their indirect coupling.[17]

The 1961 Strasboug conference was a somewhat pale reminiscence of the 1939 one. But it was the first occasion for de Gennes to present a paper. I still remember the journey from Saclay via the Vosges mountains, in a car driven by one of Herpin's group. I remember too the scathing comments by Gorter, the dutch physicist who had opposed Néel's antiferromagnetism and saw no interest in de Gennes' paper.

It is however this activity on rare earth metals which allowed me to suggest to Kittel, when we were both lecturing in Paris at a NATO summer school on solid state physics, that he extends to de Gennes his kind invitation to Berkeley he offered me when I was in Bristol. It is in that six months stay in Berkeley that de Gennes made the acquaintance of Pincus, one of his most faithful collaborators. And, according to Pincus, de Gennes spent many long hours of his stay to study the recent Russian literature on superconductivity, that would soon inspire his own work and that of the group he would develop in Orsay in the early 1960's.

It is by this work on magnetic scattering of neutrons and electrons that de Gennes was known when the occasion presented itself in 1961 for me to recruit him in the new university campus that developed in Orsay since 1956. De Gennes was thus rejoining his friend Blandin, one of my first PhD students, whom he had taken a habit of visiting in my small bureau of the School of Mines, before we moved to Orsay in the end of 1959. After an initial temptation to rejoin the high energy theoreticians who shared our building in Orsay, de Gennes put his mind completely on new fields of solid state physics; and his insistence to have in our lab in Orsay also some experimental work on the electronic structure of metals would soon lead to a large increase of activity, supported from the start by the CNRS.

4. Ferromagnetic Resonance

The idea of proposing de Gennes for a junior professorial post in Orsay was suggested to me by Abragam. They were in contact on magnetic resonance problems in ferromagnetics. A notable work, initiated in Berkeley, concerned the nuclear relaxation of iron in Yttrium iron garnets. It appears in a series of paper written with Pincus, Portis and Kittel on the fast relaxation mode and extended in her thesis by Hartmann-Boutron on the dominant slow ones.[18]

When de Gennes started teaching in our one year special training in solid state physics for future research students, he took for us the place of Philippe Meyer in an introduction to quantum mechanics; this was still missing in those days in France in the "normal" training of physics. But I also asked him to take part in a set of courses for more advanced research people that would vary over the years. This system would lead to notable courses, a number of which were published in book form, including de Gennes' later ones on superconductors and on liquid crystals. His first lectures at that advanced level were on resonance techniques applied to solid state physics, especially in ferromagnets.

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It happened that I was invited to give a general lecture on such a theme at the XIth meeting of the Ampère Colloquium, which gathered at the time the Europeans specialists of resonance. It was to be held in Eindhoven in 1962. I was then going through a time of stress in research, between writing with difficulty a second edition of my book on dislocations and rather heavy duties I had accepted from Aigrain in distributing French military money in support of fundamental research in solid state physics. I had been rightly reproached by de Gennes and Blandin to spend too little time in our lab in Orsay. Owing to a feeling of incompetency but also because of this revolt, I suggested that de Gennes should take my place while I would only treat a minor point on the Knight shift of metals. We went to Holland, de Gennes, his wife Annie and myself, in their small Citroën car, which brought us with difficulty to the top of the hills. In Eindhoven, we were very warmly received by Casimir, the scientific director of Philips with, at his side, Nozières, de Gennes' friend from Ecole Normale and son of a Philips scientist in Paris. From my closer contacts with Casimir later on, it was clear that, since that first meeting, he held de Gennes in great esteem. Indeed de Gennes was repeatedly invited to Eindhoven and, I believe, offered in a pressing way to take Casimir's succession in Philips, just before de Gennes accepted his chair at the Collège de France. Casimir was clearly a very exceptional scientific head of an industrial firm, having made a name for himself in physics before devoting his efforts to the well being of what he considered as a national treasure. His frequent personal contacts with Néel fully profited to Philips in the application of ferrites, and I think that this contact has deeply influenced de Gennes's attitude towards industrial research.

5. Conclusions

The period treated in this first chapter was for de Gennes a time of initiation to research and to research people. It does not appear in the notes he wrote yearly from 1961 onwards;[2] and indeed no paper of that time appears in the list of his publications that appeared some time ago.

I understand this feeling of not being yet his own master in choosing his field of research. But I think that period was important for two reasons.

Fluctuations near a second order phase, his initial subject, was not a simple problem; it was indeed somewhat neglected at that time, owing I believe to Landau's systematic tendency to neglect them. But by looking at how delocalized particles were scattered by local imperfections, it lead him to problems mixing together real and reciprocal spaces, in a way Guinier had met for X-rays on crystal defects and I on impurities in metals. He would systematically develop this mixed approach in superconductors and in liquid crystals, especially in problems involving free surfaces or contacts; and this is also the main theme of his studies of soft matter.

These first works also show his main qualities: quick grasp of a new problem and of its dominant features, able to lead to a useful schematization; study of possible corrections, to show the limitations of its validity more than to replace this caricature by a painstaking photography; finally ability to transfer as much as possible of its accumulated skill from old to new domains.

We have seen at the beginning the role of Sadron's thesis in Strasbourg in the ferromagnetism of transitional metals and alloys. Sadron developed after the war a lively laboratory on polymer which I had the occasion to visit in the early 60's in my work for Aigrain. Sadron was thinking at the time of possible applications of polymer physics to biophysics. He came to Orsay to give a talk on the flexibility of polymers and DNA molecules which interested de Gennes; he then tried to enlist de Gennes' collaboration to a new laboratory he was developing in Orléans on biophysics in the late 60's. But de Gennes struck a more lasting friendship with my cousin Benoit, Sadron's successor in Strasbourg, with whom he developed in Saclay a group studying by neutron scattering the concept of polymer reptation he had developed with Edwards: scientific history is not quite straightforward!

References

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