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Some requirements for a theory to explain probable room-temperature superconductivity and unusual magnetic properties of narrow channels in oxidised atactic polypropylene

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Measurements of electrical conductivity, thermal conductivity and magnetic properties of narrow channels through oxidised films of atactic polypropylene reported in the last ten years are reviewed, and reasons are given why it is thought that claims of room-temperature superconductivity in such channels in this material are valid. Five requirements for any theory which can explain all the experimental results are listed, and a discussion is given of how one candidate theory may satisfy these requirements.

Keywords: Room-temperature superconductivity; diamagnetism; metamagnetism; atactic polypropylene

Se revisan las mediciones de conductivitidad eléctrica, conductividad térmica y de las propiedades magnéticas de canales angostos a través de peliculas oxidadas de polipropileno atáctico, reportados en los últimos diez años, y se dan argumentos de porqué la afirmación de que dichas canales presentan superconductividad a temperatura ambiente es válida. Se listan cinco requisitos para cualquier teoría que quiera explicar todos los resultados experimentales y se da una discusión de una teoría que puede satisfacer estos requisitos.

Descriptores: Superconductividad a temperatura ambiente; diamagnetismo; metamagnetismo; polipropileno atáctico

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1. Summary of experimental results

1.1. Electrical measurements and thermal conductivity

There have been claims in the literature of room-temperature superconductivity in narrow channels through films of oxidised atactic polypropylene since 1988 [1], and three papers reaffirming this claim appeared in 1989, two from the Institute of Synthetic Polymeric Materials in Moscow [2,3] and one from the Ioffe Institute in what was then Leningrad [4].

The films were usually oxidised by heating in air at 100°C followed by irradiation with ultraviolet light, but some results on films oxidised by leaving for several years in air at room temperature were also discussed [1,3]. Work was mostly performed with In pressure contacts and a Cu base electrode. When the In contacts were put in various positions it was found that there were insulating, poorly conducting, and relatively highly conducting points. The first indication of possible superconductivity was that the resistance of the points with good conductivity did not depend on the film thickness, for films of up to 100 μm thickness, and was approximately equal to that of the contact directly in touch with the base electrode [1–3].

Some other interesting results of electrical measurements reported in the 1989 papers were:

(a) Changes of R by nine orders of magnitude by temperature cycling near room temperature in some samples [3].

(b) A probable upper limit of channel diameters of 2 μm from attempts to see conduction in the planes of films for closely spaced contacts [4].

(c) A separation of conducting channels of 7–8 μm in one film of 0.3 μm thickness [2].

(d) An increase of conductivity by a factor of about 250 for quite small applied pressures (≈ 70 g·cm^{-2}) [4].

(e) A slow decline in the number of conducting channels over a period of some days when magnetic fields of about 0.1 T were applied parallel to film surfaces [2].

(f) Experiments with 0.5 A currents with In contacts and 2-3 A with Cu contacts where the contacts melted permitted deductions that the high-conductivity state persisted up to above 429 K (the melting point of In) and also, from the experiment with Cu contacts, that there was no heat evolution in the polymer for current densities $j > 3 \times 10^6$ Acm^{-2} [3].

The strongest indications that channels through films of oxidised atactic polypropylene are superconducting at room temperature came from three properties reported in 1990 and 1991 [5–7]. These are:

1. Their electrical conductivity at room temperature is at least two and probably more than five orders of magnitude greater than that of Cu [5, 6].

2. The highly conducting state is destroyed in pulsed measurements above a critical current, and this destruction is not by thermal effects [6].
3. There is a negligible electronic contribution to the thermal conductivity in the channels, implying a violation of the Wiedemann-Franz law by several orders of magnitude [7].

A lower limit on the channel electrical conductivity σ at room temperature is obtained in two ways, directly from a four-probe measurement by the Ioffe Institute group [5] and indirectly from the lack of thermal decomposition in repeated pulsed-current measurements by the Moscow group [6], in combination with measurements of low thermal conductivity of channels [7]. The indirect method gives conductivities over five orders of magnitude greater than that of Cu, while the direct method gives a lower limit for σ of more than two orders of magnitude greater than that of Cu if channel diameters are assumed to have their estimated upper limit of $2\,\mu$m [4, 6], or of nearly five orders of magnitude greater than that of Cu if an estimate of the channel diameter of $0.1\,\mu$m is made by identifiying the contact resistance with a spreading resistance associated with the contact metal [5]. The violation of the Wiedemann-Franz law indicates that the channels are superconducting, rather than having ultra-high normal conductivity.

Two other properties of the channels estimated in [6] are:

4. The critical temperature for destruction of the highly conducting or superconducting state satisfies $T_c >$ 700 K.
5. The critical current density $j_c \sim 5 \times 10^9$ Acm^{-2}.

1.2. Magnetic properties

We now come to magnetic properties. There are three anomalous magnetic properties that need explaining:

1. What is called "anomalous ferromagnetism" by the Moscow group, but which should perhaps be called metamagnetism, with a transition field in the range of 0.1 to 0.2 T, seen in well oxidised films [8].
2. Large diamagnetism at low applied fields in about 10% of films studied [3]. The diamagnetic susceptibility at low fields H is approximately proportional to $(1/H)$ [9].
3. Occasional spontaneous forces tending to push samples towards lower fields in inhomogeneous magnetic fields [10].

Study of the third property requires a criterion for whether a spontaneous force is significant enough to be worth counting. Three criteria were chosen, based on strength, duration and rate of growth. Five events satisfying the required criteria occurred over a few hundred hours viewing time for fields in the range of 80 to 400 Oe, but none for zero field or for fields greater than 800 Oe. All five events gave forces pushing the samples towards lower fields, corresponding to diamagnetism.

It is probable that both properties 2 and 3 are associated with what happens when conducting channels join up at their ends to form closed loops. This was first suggested by the Moscow group for property 3 in 1993 [10].

2. Why conducting channels exist

Grigorov *et al.* [11, 12] argue that conducting channnels are likely to exist in any elastomer (material with very low elastic constants) which contains a sufficient concentration of rotatable electrical dipolar groups. In an elastomer an extra charge can orient all dipoles within some radius R_0 given by

$$R_0 = (eD/\pi v G \epsilon_\infty)^{\frac{1}{2}}. \qquad (1)$$

Here D and v are the dipole moment and volume of the group, G is the shear modulus of the material, and ϵ_∞ is the high-frequency dielectric constant. Assuming $D \approx 3$ Debye, $v \approx 0.1$ nm^3, $\epsilon_\infty = 2.2$, and that G lies in the range 4–100 MPa, we find $R_0 = (3 \pm 2)$ nm.

In such an elastomer material Grigorov *et al.* [11, 12] estimate:

(a) It is energetically favourable for some atoms to ionise, with ions and electrons both surrounded by regions of aligned dipoles, provided that there are three or more dipoles in any region of radius R_0. An electron plus its surrounding region of aligned dipoles is an unusual type of polaron.

(b) If the static dielectric constant is more than a few times ϵ_∞, it is energetically favourable for polarons to join up in pairs, and then in long strings called "superpolarons". Current carriers can move up and down the strings fairly freely.

The estimated diameter of the superpolaron strings is of the order of a nanometer, but diameters of conducting channels have been inferred from experiments [4–6] to be in the range 0.1 to 2 μm, and so it has to be postulated that the strings or filaments combine in quite large numbers to form conducting channels.

3. Some requirements for a theory to explain both superconductivity and magnetic properties of channels

1. Assuming a pairing theory, we need large pair binding energies, at least 0.1 eV for room-temperature superconductivity, or at least 0.2 eV for superconductivity at 700 K, supposing that pair binding energies need to be at least about $4k_{\mathrm{B}}T_c$.

2. We need either small pair effective masses, at least in the direction along the channels, or an unusual pair dispersion relation [13]. Otherwise the Bose–Einstein condensation temperature T_B of bosons will limit T_c to fairly small values.

We have made calculations of T_B for non-interacting bosons for the case of quadratic dispersion relations characterised by different masses M_L and M_T parallel and perpendicular to filament directions in an array of filaments [14]. If the transverse cut-off energy W_T associated with the minimum filament separation is smaller than $k_B T_B$, we find from numerical results for three cases with differing ratios $(k_B T_B / W_T)$ that, for a sufficiently large number of filaments,

$$k_B T_B = (4.5 \pm 0.3) \frac{\hbar^2}{2(M_L M_T)^{\frac{1}{2}}} \frac{c}{a_T}, \tag{2}$$

where c is the linear carrier concentration in a filament, and a_T is the filament separation. If, *e.g.*, $c \approx 10^7$ cm^{-1} and $a_T \approx 2$ nm, then, to obtain $T_B = 700$ K we need an average mass of about $1.4\, m_e$. Since transverse masses are probably fairly large, small longitudinal boson masses would be needed in this type of model.

3. In order to explain $\chi \propto (1/H)$ in samples showing diamagnetism, which implies magnetic moments independent of H, we probably need large circulating supercurrents to arise whenever channel ends join to form a closed loop.

4. We need to explain why the direction of such currents is such as to give magnetic moments in the direction opposite to that of the applied field, in both susceptibility and spontaneous-force measurements.

5. We need to explain metamagnetic transitions for magnetic fields in the range of 0.1 to 0.2 T.

4. Possible theories

4.1. High-drift-velocity model

This model was introduced in 1994 [15, 16], and is based on an old idea of Parmenter [17] that enhancements of electron-electron attractions can occur at drift velocities close to the velocity of sound or to a phase velocity of whatever excitation is mediating the attraction. Consequences of the model for magnetic properties are discussed in [18]. A discussion of how this model deals with the five points mentioned in the previous section is given below.

1. Pair binding energies may be large because of the enhanced interactions at special drift velocities mentioned above. For Fermi energies small compared with the energy $\hbar\omega$ of whatever mediates the pairing, this enhancement becomes infinite for quasi one-dimensional systems in the simplest perturbation approach to electron-electron attractions [15, 16]. It was suggested in [16] that plasmons of energy ~ 1.8 eV might mediate the attraction. For some discussion of what may happen beyond perturbation theory see point 2 below.

2. Effective masses of pairs, inversely proportional to the curvature of the energy, E, *versus* center-of-mass wave vector K for pairs, could be small if E were to go through a sharp minimum at some optimum K. Preliminary calculations for bipolarons in one-dimension using a variational method appropriate for intermediate coupling strengths and the assumption that bare electrons have a constant effective mass do not support the idea of a second minimum in E at $K \neq 0$. However, after inclusion of a conjectured approximate method of treating effects of band energies for bare electrons proportional to $[1 - \cos(ka)]$, where a is the lattice constant and k is an electron wave number, it seems that, for some coupling constants, the bipolaron energy can go down to a cusp-like minimum for K equal to its maximum possible value, $K_m = 2\pi/a$. Thus there may be an unusual dispersion relation. From the numerical calculations we have done up to now, it appears that there will be an approximately linear dependence of energy on wave vector measured from K_m near K_m, becoming sublinear further away. If electric currents from pairs with particular wave vectors are proportional to dE/dK, then, for a linear dispersion relation, there would be two types of pairs with equal and opposite large velocities, although the state at the cusp will presumably consist of a superposition of states with equal and opposite velocities. With no external perturbation, a condensate with states at the cusp with zero net velocity may be expected. However, the degeneracy of the two states from which the zone-edge cusp state is composed will be broken by an external perturbation such as an applied current for a quasi one-dimensional filament with end connections, or a magnetic field for a filament in the form of a closed loop. Then, since exchange interactions make a superposition of two condensates from nearly degenerate states energetically unfavourable [19], we expect that a state with a high current density in one of the two directions will be preferred. Even for a linear dispersion for a single quasi-one dimensional filament, we need to invoke interaction between filaments within a channel in order to obtain a finite condensation temperature.

3. Large circulating currents can occur in closed loops, since high drift velocities ($\sim$ a few times 10^7 cm·s^{-1}) were preferred in the original model [16], and, for appropriate strengths of electron-boson coupling and energies of the bosons which induce pairing, drift velocities can be of this order too in the bipolaron theory with a cusp-like minimum in the pair energy at the zone edge.

4. A possible explanation as to why the initial direction of the circulating currents may be such as to oppose the applied field is as follows. To close a loop, on average the material of the loop has to move more towards than away from the center, and one can thus invoke Lenz's law as applied to moving wire segments to show that the induced e.m.f. for this motion

is such as to cause currents with a direction of circulation which produces a field opposite to the applied field.

An alternative possible explanation more dependent on details of the high-drift-velocity model was given in [18].

Whichever explanation is invoked for the initial current direction, it is expected that, in due course, the loop as a whole may rotate so that its moment becomes parallel to the field, on a time scale which will decrease as the applied field increases. A reversal from diamagnetism to paramagnetism was reported in [1, 10] in a 1600 Oe field on a timescale of the order of a minute.

5. Metamagnetism in the model is associated with a transition from an antiferromagnetic to a ferromagnetic array of elementary long-thin current loops. To explain a transition field of e.g. 0.12 T, we need about 30 filaments per current loop [18].

4.2. Model with exchange-induced triplet pairing

There is very little published on this model yet, which was mentioned in [12], and so it is difficult to assess its plausibility at present.

5. Conclusions

There is experimental evidence for superconductivity and unusual magnetic properties in narrow channels through films of oxidised atactic polypropylene. Although not discussed here, there is also evidence that some of the same unusual properties are present in films of polydimethylsiloxane [20, 21]. Only one candidate theory to explain all types of data has been published in any detail [15, 16, 18], and this theory needs more work for its justification beyond perturbation theory.

More groups should try to reproduce and extend the Russian experimental work. Some suggested worthwhile experiments are listed in [18].

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