Search for high-temperature superconductivity[1)]

E. K. Zavoĭskiĭ

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Contactless methods are proposed for the detection of superconductivity in microregions of specimens whose structure is simulated and interpreted by a special computer program.

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The theoretical advances of the last few years have enabled us to map out different ways of approaching the problem of high-temperature superconductivity.[1] There is, however, a considerable gap between theory and practice, which can be filled only by a "quasi-infinite" experiment or by some new developments in the theory. We shall describe contactless experimental methods that can be used in searches for high-temperature superconductivity, in which a limited number of measurements will yield substantial statistics on the variation in parameter values and experimental conditions, thus approaching the "quasi-infinite" experiment.

The principle of the method is to record superconductivity in microregions V_0 of specimens of volume $V \approx 1$ cm^3. This enables us, with the aid of a computer, to generate a special specimen structure in which the number of variations of local parameters is of the order of $N \approx V/V_0$. Theoretical predictions must then be taken into account in the selection of structures. If microsuperconducting regions are found, we have to establish the conditions under which they appear. However, it will be shown later that this is relatively a simpler problem than the direct search for superconductivity in microspecimens.

Our numerical estimates of the possibilities of the method were based on the assumption that high-temperature superconductivity might arise at least in microregions with characteristic linear dimensions of up to 10^{-4} cm although this limit does not restrict the sensitivity of the method.

1. METHODS

a) This group of methods is based on the principle of contactless detection of microsuperconducting regions. Let us suppose that these regions can be represented by toruses or disks with nonsuperconducting regions at the center. If the specimen is prepared in a uniform magnetic field H, then, when the field is reversed, the magnetic flux inside the superconductor will persist (the case where this condition is not satisfied is considered separately) and the specimen will experience a couple given by

$$M = \int JHr\, dl, \tag{1}$$

where J is the current in the superconductor, r is a characteristic linear dimension of the region, and dl is an element of length. A specimen held on a sufficiently thin suspension will therefore rotate under the action of the couple

$$M = H^2 r^3. \tag{2}$$

Let us calculate the number of rotations of the specimen. The period of torsional oscillations is

$$T = 2\pi \sqrt{\frac{I}{k}},$$

where I is the moment of inertia of the specimen and k is the elastic constant of the suspension. Since $M = k\alpha$, where α is the torsional angle, we have

$$r = \left(\frac{4\pi^2 I\alpha}{T^2 H^2}\right)^{1/3} = \left(\frac{\alpha k}{H^2}\right)^{1/3}. \tag{3}$$

This formula can be used to determine the radius of a superconducting region corresponding to $\alpha = 1$ for given values of k and H. The choice of H should be dictated by the condition for superconductivity, i.e., H must be less than the critical field H_c corresponding to a superconductor of linear dimensions r at a given temperature. Moreover, the magnetic flux $\pi r^2 H$ must not be less than $\Phi_0 = \pi\hbar c/e = 2.07 \times 10^{-7}$ G·cm^2 (the quantum of the magnetic flux). When this condition requires that $H > H_c$ (this may occur for very small r), the choice of the computer program for calculations on the specimen will require the specification of values of r for which $H < H_c$. Such structures will be discussed below.

The minimum value of k corresponds to the minimum weight of the specimen if we do not take into account the limits set by fluctuations of suspension and medium (gas) in the measuring device. However, if we reduce the size of the specimen, this will automatically reduce the statistics of the measurements because the value of N will be reduced for given characteristic radius r. At the same time, if the experiment shows that there are superconducting regions with characteristic linear dimensions $r_{min} < r$, transition to specimens of small weight will enable us to reduce the thickness of the suspension without reducing N. On the contrary, this will result in an increase in N. This follows from the following considerations. The maximum admissible weight P of the specimen is related to the cross-section area s_0 of the suspension thread by $P/s_0 = C$, where C is a constant for each material of the suspension thread and the exponent n_0 in the elastic constant $k = k_0 s_0^{n_0}$ of the suspension can be approximately set equal to 2. Hence, using

[1)]This paper by E. K. Zavoĭskiĭ was written shortly before his death. It represents one of his scientific interests during the latter period of his life. It is hoped that it will be of interest to our readers. (Editorial Board)

(3) and assuming that the specimen of density ρ is spherical in shape with radius r_0, we have

$$r=\left(\frac{\alpha k}{H^2}\right)^{1/3}\sim k^{1/3}\sim\rho^{2/3}R_0^2,\quad N\sim\frac{1}{\rho^2R_0^8}\sim\frac{1}{\rho P}.$$

We note that, as r decreased, the couple given by (1) and (2) can be substantially decreased because of the decrease in the critical field H_c. The experiment must then be performed for $H<H_c$ with $H=H(r)$ in (3). The limit of the sensitivity of the method will therefore also depend on the critical field $H_c=H_c(r)$. Naturally, any search for superconductivity in regions with the minimum size r_{min} must be carried out in specially prepared fine-structure specimens (see below).

In nonequilibrium processes, and in certain other cases, the superconducting current may become attenuated. The attenuation in the force couple M, if established experimentally, may then serve as a good indicator of the nature of the phenomenon.

We must mention two further points in connection with the validity of (2) and (3). They are: 1) these formulas were obtained on the assumption that the specimen was prepared in a field H which was then reversed without changing its numerical value. Equations (2) and (3) therefore include the square of the field. However, if the specimen has already been prepared in a field H_0 and is then placed in a uniform field H' which is also reversed, the couple will be proportional to H_0H' provided neither field exceeds the critical field mentioned above. 2) Since a strong magnetic field $H>H_c$ will destroy superconductivity, the reduction of H below the critical value in the superconducting ring should be accompanied by the capture of magnetic flux $\Phi=sH_c$ by the superconducting ring, where s is the area of the nonsuperconducting region surrounded by the superconductor. Hence, it follows that the "preparation" of the specimen can also be performed in this way.

Finally, we note that the experimental method can be used to carry out the measurements at any temperature.

b) The above method presupposes that the attenuation of the currents in the microvolumes is sufficiently small, so that there is enough time for the measurements to be carried out. However, the measurement period may turn out to be quite large, especially for thin suspensions. We shall therefore consider a measurement procedure which has lower inertia. Consider a specimen in the form of a sphere, cube, or plate and suppose that three or more piezoelectric transducers are attached along the coordinate axes. The specimen is placed in a uniform alternating magnetic field $\tilde{H}=H_0\sin\Omega t$. Depending on the direction of H_a relative to the plane along which the piezoelectric probes are cut, longitudinal or acoustic sound waves will be excited by the force $f=\int JHdl$ on the microsuperconducting region due to the magnetic field H. If the attenuation time of the superconducting current is comparable with $2\pi/\Omega$, there will be a phase shift between H and the acoustic wave, which can be measured. This can be used to establish the coordinates of the superconducting region, and the current attenuation time for this region. If, on the other hand, the attenuation time is much greater than $2\pi/\Omega$, then, by preparing the specimen in a constant magnetic field, as described in Sec. 1, it is possible to carry out the same investigations as in the case of the sensitive suspension but, in addition, the coordinates of the superconducting region can be determined.

If it is desired to determine the coordinates with a high degree of precison, it is essential to use high frequencies Ω so that the wavelength of the acoustic oscillations is much smaller than the linear dimensions of the specimen. Moreover, it is possible to use modulated high-frequency fields with periods of the order of the time taken by the acoustic waves to traverse the specimen. However, the precision of the localization cannot exceed about a quarter of the wavelength of the acoustic wave. Therefore, for example, when $\Omega/2\pi=10^7$ Hz, the localization limit in nonmetallic specimens, with small sound scattering by inhomogeneities, turns out to be about 4×10^{-3} cm. For well-conducting solid metallic specimens, high frequencies cannot be employed because of the small skin depth. In this case, the specimen may be in the form of layers separated by dielectrics.

2. ROLE OF MAGNETIC FIELD AND SPECIMEN HOMOGENEITY

The homogeneity of the magnetic field and its strength determine the sensitivity limit of the method, i.e., the minimum size of detectable superconducting region. This is clear from (2) and from a consideration of the forces acting on a specimen in a nonuniform magnetic field. It is well known that the force acting on a body with local susceptibility $\chi(x,y,z)$ is given by

$$F=\int\limits_V\chi(x,y,z)H\nabla H\,dm,$$

where the integral is evaluated over the volume V of the body. Hence, it is clear that the couple acting on the body may be due to inhomogeneity in χ, to deviations of the shape of the specimen from a body of revolution, or a shift of the axis of revolution from the symmetry axis of the body. Numerical estimates of these effects can easily be carried out and checked experimentally. Comparison of the moment of the force F with the couple M calculated from (2) can be used to determine the admissible gradient of H. Estimates show that the necessary homogeneity of the magnetic field can be achieved in modern electromagnets.

3. ROLE OF FERROMAGNETIC CONTAMINATION

It is easily verified that even small ferromagnetic contamination (the radius of the ferromagnetic speck can be of the order of the radius of the superconducting region calculated above) will mask the true behavior of the specimen. The impurity may appear as a result of accidental contamination or during the preparation of the specimen from the required components.

Ferromagnets are usually characterized by high Curie temperatures and by hysteresis, and this facilitates their identification. However, in magnetic fields exceeding the coercive force H_{co}, the behavior of the specimen will be very different from the situation in which it contains a superconducting region. As soon as the external magnetic field exceeds H_{c0}, the behavior of the specimen will be typically that of a ferromagnet, i.e., a rapid reversal of H will not be accompanied by the appearance of a couple since the ferromagnet will reverse it magnetization before it succeeds in rotating. Moreover, there is a substantial change in the period of the torsional oscillations of the specimen, due to the appearance of additional forces that orient the magnetic moment of the ferromagnet in the external magnetic field, especially in a strong magnetic field.

Finally, we note that the presence of ferromagnetic contamination (with both small and large coercive force) can be detected by observing the ferromagnetic resonance in ready-made specimens. It is well known that the position of the resonance lines is characteristic for ferromagnets, and this can be used to judge the presence of impurities quite reliably. The sensitivity of modern radiospectrometers is sufficient for the detection of microferromagnetic contamination.

We note that the search for ferromagnetic resonance can be carried out both with the suspension apparatus[2)] and by observing the rotation of the specimen in ferromagnetic resonance. [2] It is readily verified that, if the sensitivity of the suspension is sufficient for the detection of ferromagnetic impurities, then, for the given level of the high-frequency signal, it will also be sufficient for the detection of ferromagnetic resonance. Thus, we have a simple radiospectroscopic method of separating superconducting and ferromagnetic microregions. However, this method is inconvenient for specimens whose thickness is greater than the skin layer depth. In such cases, we must proceed as described above.

4. OTHER SIDE EFFECTS

Closed electrical currents may appear in nonuniform specimens in which reactions due to chemical interactions between the components may take place under certain conditions, the currents being due to gradients in concentration, and so on. Such currents will interact with the magnetic field and will give rise to the rotation of the specimen when the magnetic field is reversed. However, the current will, as a rule, vanish when the temperature and time are reduced. Moreover, the angle of rotation of the specimen will be proportional to H and not H^2 (as for the super conducting region), there will be no critical value H_c of the magnetic field, and so on.

Similarly, any change in the magnetic field in an inhomogeneous specimen may result in polarization effects on the boundary between different phases, which is equivalent to the appearance of electromotive forces, and, therefore, currents. However, polarization currents should rapidly decay once the magnetic field is established, especially if the specimen is a good conductor.

5. STRUCTURE ELEMENTS AND IDENTIFICATION OF EXPERIMENTAL RESULTS

Ideally, the data fed into the computer for a set of materials of interest to us should lead to a model of the structure of the specimen in which any change in the parameters leads to a completely defined combination of materials in any cell of the specimen for the maximum possible number of cells $N = V/V_0$, where the cell and specimen volumes, V_0 and V, are given arbitrarily.

Once this structure has been computed, the real specimen is made and placed in the magnetic field. The final preparation of the specimen should take place during the variation of one (or several) parameters (for example, temperature, pressure, solubility, freezing, and so on). Let us take the temperature as an example. Suppose that the specimen contains materials that can be melted down. The temperature can, therefore, be raised above the melting point of one or several of the components, and maintained at this value. It can then be reduced below the melting point, the specimen can be transferred to the measuring system, [3)] and the temperature can be varied again (for example, it can be reduced). While this is going on, one can check whether the specimen contains superconducting regions. This procedure should be repeated several times and both the heating and the time for which the specimen is held at the higher temperature should be varied. If the presence of superconductivity is detected in the specimen in any of these cases, the computer, as it follows all the experimental parameters, should be able to specify the conditions necessary for the appearance of superconductivity by relating it to the formation of a new phase in the specimen.

This is the situation in the ideal case. In practice, one cannot always specify precisely all the properties of the initial materials, or provide an accurate calculation of the structure of the real specimen. Therefore, both the calculation and experiment will produce regions in which neither the composition nor the parameter values will be known, and this may require additional studies of the properties of the specimen components, or precise localization of superconducting cells, as well as direct investigation of their composition and structure by other methods. Nevertheless, whatever the percentage of regions with uncertain composition, the problem of finding the conditions for the formation of superconducting cells can be solved in the course of a relatively small number of experiments. For example, the following sequence of measurements can be performed for this purpose: 1) by varying the main parameters, for example, temperature, the maximum effect is produced; 2) the reproducibility of the results is verified; 3) one or several of the materials making up the specimens are excluded, so that the particular component producing the superconductivity can be identified; 4) a computer is used to guide toward experiments with increasing structural elements and, finally, a multistructure specimen that can be investigated by ordinary methods is prepared.

The total cost of facilities and man-hours expended in this kind of investigation is several times less than the cost of a direct search for superconductivity in macroscopic specimens. Moreover, each individual experiment carried out in the above way will provide a greater

2) The constant magnetic field must then be parallel to the suspension thread.

3) The entire process of temperature variation can also be carried out in the measurement apparatus.

amount of statistical data even when it does not lead to a positive result. It is, therefore, necessary to store in the computer memory all the systematic experimental procedures, so that a data base for this problem can be established. This data base will eventually transform the empirical character of the search into a systematic procedure and will, therefore, lead to a generalization.

It is interesting to note that searches for superconductivity do not always require the identification of conditions for the appearance of superconductivity. This is so because experiment enables us to determine the main parameters of the superconducting state, such as the critical temperature, critical magnetic field, and, under known conditions, the resistivity. Thus, for example, if it turns out that the critical temperature is too low, this case is of purely physical and not practical interest, and need not be investigated in detail any further.

Let us now consider some of the structure elements. Structure should be determined by the specific experimental problem, the possibilities of the computer, and the specimen fabrication technology. Only a few examples of simple structure elements are therefore given below.

For many structures, it may turn out to be desirable to introduce "voids" in the form of filaments (for example, filaments of quartz, nonsuperconducting metals, and so on), the radius of which will specify the minimum linear dimensions r of the regions surrounded by the superconductor. The introduction of nonsuperconducting voids into microsuperconducting regions is a way of using a highly reliable contactless measurement method.

Consider this type of structure element in a search for superconductivity in doped semiconductors and metal alloys. Suppose that the initial semiconductor (metal) is located between two parallel plates made of two materials which dope the semiconductor as the temperature is increased. Let us suppose further that a quartz filament passes from one of the plates into the other in the direction of diffusion. It is clear that at each end of the thread the concentration of one of the materials is high and the concentration of the other is low. The absolute value of the concentration depends on temperature and time. Therefore, if superconductivity appears for a particular degree of doping in the given segment of the filament (for example, after cooling), the external magnetic field will be frozen into the cross section of this segment of the suspension, and can be investigated by one of the above methods. This simplified model of the structure element can be considerably extended by the simultaneous introduction of a large number of dopants, but with the two-plate system replaced by three-dimensional structures with a large number of nonsuperconducting threads. However, in principle, such a structure may not contain the threads which must, therefore, be looked upon simply as a way of simplifying the calculations and the methods of practical preparation of specimens, if we are not interested in studying the superconductivity on the boundary between the thread and the ambient medium. In the last case, the thread is the active element and can be made by special technology from selected materials. This type of thread (or thin capillary) may contain materials which diffuse into the ambient medium when heated, producing doped regions or multicomponent alloys, and so on. The thread performs here two functions, namely, it forms new combinations of materials and, secondly, it acts as a void inside the superconductor.

We now consider another simplified problem, namely, a sphere of radius R placed in a liquid in close proximity to n centers of materials, $A_1, A_2, \ldots, A_n$, which begin to dissolve at time $t=0$. This combination of a sphere and n material, in which the parameters of both the soluble media and of the medium of the sphere can be varied, can be repeated many times throughout the specimen when R is sufficiently small. Moreover, not all n materials are necessarily different, and R may be different for different spheres. It may even be equal to zero.

Such structures can be used in the case of dissolution and mutual diffusion of metals (at the appropriate temperatures), doped semiconductors, studies of processes occurring on the boundaries of different media, liquid and frozen solutions, solvents, and so on.

6. CONCLUSIONS

Computer simulation of special structures in which one or more parameters (for example, temperature, solvent concentration, evaporation, pressure, sorption, and so on, and also nonequilibrium states) are varied, produces the successive development of local substructures with a quasi-infinite number of combinations of compositions, contacts, concentrations, and so on, and this can be used to organize a broad search for materials with required properties. The first among them are the high-temperature superconductors.

Complete identification of the conditions for the appearance of microregions with superconducting properties requires a relatively small number of experiments and repeated computer simulations. The next step is to prepare a specimen with specified properties but, at this stage, with much larger dimensions, so that it can be investigated by conventional methods.

Estimates show that, even in a single experiment, such methods can be used to investigate 10^6-10^9 combinations of multicomponent compositions.

In some ways, the method resembles the "biological experiment" in nature, but is substantially restricted by the relative simplicity of the problem, small volume of the media, the use of great computer power, and the fact that it is guided by the modern theory of superconductivity.

The development of high-temperature superconductors is one of the central problems in thermonuclear fusion.

[1]V. L. Ginzburg, Usp. Fiz. Nauk 118, 315 (1976) [Sov. Phys. Usp. 19, 174 (1976)].
[2]A. Kastler, transl. in: Paramagnitnyi rezonans (1944–1969) [in: Paramagnetic Resonance (1944–1969)], All-Union Jubilee Conference, Nauka, Moscow, 1971, p. 9.

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