New Criterion for Superconductivity in Metals

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A criterion for the occurrence of superconductivity based on the (average) freedom number f of the free electrons in the metal is proposed and applied to the nine superconductors and twelve nonsuperconductors for which the freedom number can be calculated on the basis of the available information. For all the superconductors the freedom number lies between $+0.15$ and -0.16 and, while it is equal to 0.14 for one nonsuperconductor, it lies outside these limits for all the other nonsuperconductors. The quantity $\gamma=(n/n_f)f$, where n_f/n is the number of free electrons per atom, can be calculated for a larger number of elements (14 superconductors and 27 nonsuperconductors) than f. A criterion based on this quantity is still fairly successful for elements with normal Hall effect and somewhat less successful for elements with anomalous Hall effect. A comparison of the proposed criteria with criteria due to Kikoin and Lasarew, Fröhlich, and Bardeen shows that the criteria based on f and γ are more successful.

A NUMBER of attempts have been made to relate on an empirical basis the ability of a metal to become superconducting with other properties. One of the most successful of these was that of Kikoin and Lasarew[1] who found that both the magnitude of R, the Hall coefficient at room temperature and its product with the conductivity σ at room temperature, are in general smaller for superconductors. Figure 1(a)[2] shows on a pair of logarithmic scales the value of the quantity $|R|\sigma$ (which provided the better correlation) in the case of elements with normal ($R<0$) and anomalous Hall coefficients ($R>0$). Here, and in the rest of the figure, superconductors are listed to the left of the scale while nonsuperconductors are listed to the right.

In view of the recently discovered isotope effect,[3,4] it is now accepted that the occurrence of superconductivity is due to the interaction of the conduction electrons with the lattice vibrations. More specifically, according to the theories of Fröhlich[5] and Bardeen,[6] this interaction leads at the transition temperature to a change of the state of the electrons near the Fermi surface. Each of these investigators has given a criterion for determining whether this interaction is strong enough to lead to superconductivity in any given element. For this purpose, Fröhlich introduced the quantity α,

$$\alpha=0.5\frac{(n_f/n)^{5/3}\rho n}{\rho_{\mathrm{Ag}}n_{\mathrm{Ag}}}, \tag{1}$$

where ρ is the resistivity, n and n_f are the number of atoms and of free electrons, respectively, per unit volume of the element in question, and ρ_{Ag} and n_{Ag} are the values of ρ and n for silver. His criterion, which is not supposed to apply for transition metals or metals of the Bi group, is that α be greater than one for superconductors and smaller than one for other metals. Figure 1(b) shows the quantity α on a logarithmic scale for the elements for which the criterion is applicable. Fröhlich consistently took the factor (n_f/n) as being equal to one in computing α and we have done likewise in preparing Fig. 1(b). It should be mentioned that the correlation is not improved if the usually quoted values of n_f/n are employed. Bardeen's criterion, which is not supposed to apply to transition elements, is simply that β, which is defined by

$$\beta=\nu\rho n,$$

where ν is the chemical valence taken as being equal to the group of the element in the periodic table, is larger than 10^6 for superconductors and smaller than 10^6 for nonsuperconductors if ρ and n are expressed in electrostatic cgs units. Although, as just remarked, this criterion strictly does not apply to transition elements, he included those transition metals which are superconductors in testing its validity. In preparing Fig. 1(c), which shows the value of β on a logarithmic scale, we did likewise.

It is apparent that the criterion of Kikoin and Lasarew is more successful than those of Bardeen and of Fröhlich. The question thus arises whether the quantity $R\sigma$, considered by the first investigators, might not be related to some more basic parameter measuring the interaction between the electrons and the lattice. It has occurred to us that the (average) freedom number f is such a parameter. We have

[1] I. Kikoin and B. Lasarew, Nature **129**, 57 (1932).
[2] The following remarks apply to all the parts of Fig. 1. Unless it is stated otherwise, all the metals for which the required information is available in the literature were included. In each case, the most recently published values of the quantities required were used. The value of the resistivity of yttrium was kindly supplied prior to publication by Dr. F. H. Spedding, Ames Laboratory of the U. S. Atomic Energy Commission. The values used for Sn are those characteristic of the tetragonal form. Since mercury is not solid at room temperature the Hall coefficient used was that measured at -60°C and the "room temperature" value of the conductivity was derived from the values below the melting point using the relation $\sigma\sim 1/T$.
[3] Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).
[4] E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950).
[5] H. Fröhlich, Phys. Rev. **79**, 845 (1950).
[6] J. Bardeen, Phys. Rev. **80**, 567 (1950).

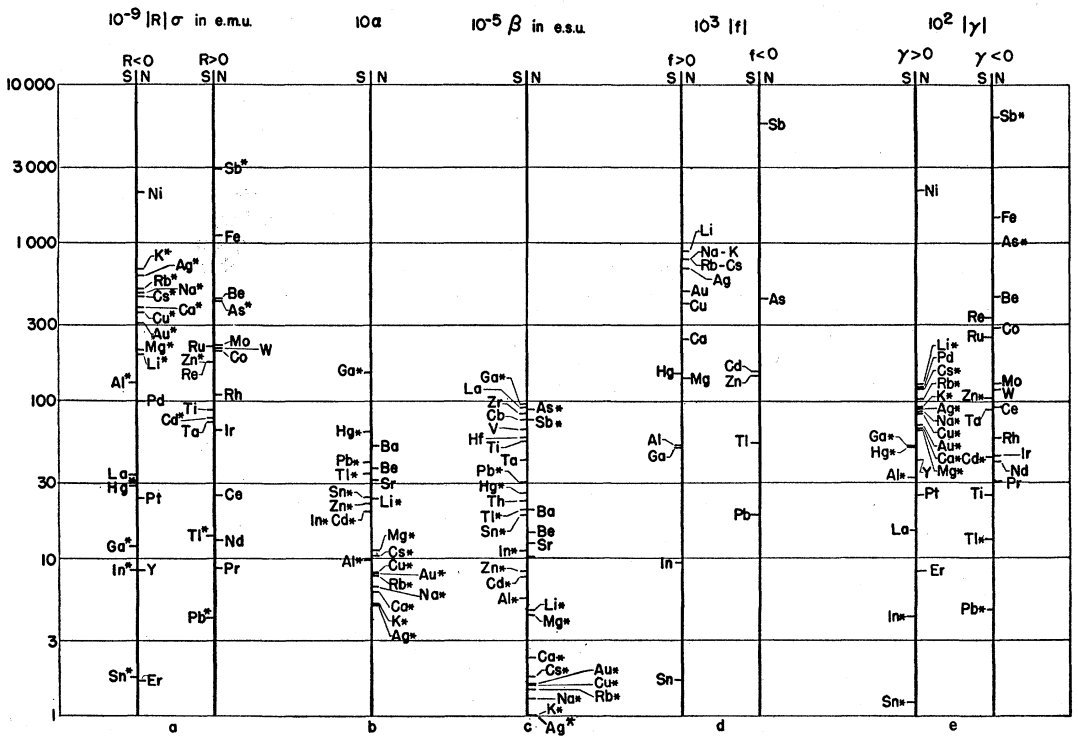

FIG. 1. Rrepresentation of various proposed criteria for the occurrence of superconductivity (a) Kikoin and Lasarew, (b) Fröhlich, (c) Bardeen, (d) and (e) present communication. The elements appearing in (d) are starred in the other parts of the figure. Elements with normal Hall effect are listed on the left-hand scale in (a), (d), and (e).

calculated f from the relation[7]

$$f=n_f eR/c, \tag{3}$$

where R is the (room temperature) Hall constant,[8] e is the (negative) electron charge, and c is the velocity of light. The values of n_f used here for the alkali metals and for Cu, Au, and Ag were obtained from the results of measurements of the refractive index and optical absorption coefficient.[7] With the exception of Be and the transition elements for which the following rule is not valid, the quantity n_f was obtanied for the other metals from the semiempirical relation[7]

$$n_f=nZT/(1650\rho A\Theta^2), \tag{4}$$

where Θ is the Debye temperature, ρ is the resistivity at the absolute temperature $T(\gg\Theta)$, and the other symbols have the conventional meanings. Figure 1(d) shows, on a pair of logarithmic scales, the absolute values of the freedom number thus obtained for metals with positive and negative freedom numbers. It can be seen that for the elements shown the freedom numbers of the superconductors lie between $+0.15$ and -0.16; while with the exception of Mg (for which $f=0.14$)[9] the nonsuperconductors have freedom numbers larger in magnitude than those for any of the superconductors. To expedite comparison between the present criterion and the others shown, the elements contained in Fig. 1(d) are starred in the rest of the figure. The result that $|f|$ is small for superconductors simply means that there is for these elements a strong interaction between certain of the electrons near the Fermi surface and the lattice. Thus, a small value of f ordinarily results if the Fermi surface intersects a Brillouin zone boundary so that electrons on either side of the crossing make opposite contributions to f. The existence of such an intersection, in turn, implies the strong interaction mentioned.

It was found that the value of n_f/n as estimated in the way described does not change too fast from element to element for those metals which have a freedom number in the vicinity of the critical values, i.e., near $f=\pm 0.15$. It seemed reasonable, therefore, to use instead of f the quantity $\gamma=(n/n_f)f$ which can be calculated for a considerably greater number of elements. Figure 1(e) shows on a pair of logarithmic scales the value of this quantity for metals for which it is

[7] See, e.g., H. Fröhlich, *Electronentheorie der Metalle* (Verlag Julius Springer, Berlin, 1936), Chaps. II and III.

[8] The room temperature value was used because in the absence of extraneous effects R is temperature independent and because many Hall coefficients are available only for this temperature. (See, however, reference 2 with regard to Hg.)

[9] The occurrence of this exception may be a consequence of the uncertainties in the values of f as obtained here.

positive and negative. It can be seen that considering the larger number of metals included, the degree of separation achieved between the two classes of metals is still fairly good. The value of γ lies between $+0.5$ and -3.4 for superconductors. The only nonsuperconductors for which γ lies in this range are transition elements which are excluded from all the other criteria except the one by Kikoin and Lasarew which is based on the value of $R\sigma$. A comparison of Fig. 1(a) with Fig. 1(e) shows that the degree of overlapping for γ is, however, smaller than that in $R\sigma$. In conclusion it can be said that the criterion suggested here [Fig. 1(d) and 1(e)] is more successful then any of the others shown in Fig. 1.

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Reversible Susceptibility of Ferromagnetics*

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An expression is given relating the magnetization dependence of the reversible susceptibility normal to the field direction to that of the parallel reversible susceptibility. Modification of these susceptibility dependences due to the trapping of domain walls in metastable positions by potential holes is considered. The macroscopic magnetization is expressed in terms of a distribution of potential holes by an argument analogous to that of a "mean free path." The desirability of further examination of this approach is discussed. The reversible susceptibilities of three ferrite specimens were measured and found to compare favorably with the theory.

I. INTRODUCTION

IF one defines a susceptibility by the expression

$$\chi_r = \lim_{\Delta H \to 0} \frac{\Delta M}{\Delta H}, \tag{1}$$

when ΔH has a sense opposite to that of the change in H which brought the specimen to the point (M,H), the parallel reversible susceptibility χ_{rp} is defined in the usual manner. When ΔH is perpendicular to the direction of H, the transverse reversible susceptibility χ_{rt} is defined. If ΔH is in the same sense as the last change in total H, the differential susceptibility χ_d is defined. χ_d contains an irreversible component, χ_{rt} and χ_{rp} do not. The initial susceptibility χ_0 is defined as:

$$\chi_0 = \lim_{M \to 0} \chi_{rp}. \tag{2}$$

The parallel reversible susceptibility in ferromagnetic materials has been the subject of several authors since it was discussed by Gans[1] in 1911. A recent paper by Tebble and Corner[2] includes a general review. An expression for the transverse reversible susceptibility, given by Grimes, Orr, and Winsnes,[3] is developed in this paper. Experimental data are given for both reversible susceptibilities.

To develop expressions for these susceptibilities in terms of the magnetic parameters of a specified system, it is necessary to use different models, depending upon the particular calculation being considered. The models are altered as necessary in the following discussion. The justification for this procedure[4] is that the susceptibilities depend upon the statistical distribution of potential holes and the relative energy magnitudes involved. It presumably matters little what the specific assumed model is so long as the proper energy relations are maintained.

II. THEORETICAL DEVELOPMENT

A. The Initial Susceptibility

From measurements of the permeability spectrum using particle sizes down to the order of single domains, Rado, Wright, and Emerson[5] have shown convincingly that the low-frequency initial susceptibility of ferrites is caused primarily by wall movement rather than by rotational processes. It is therefore of interest to note how this susceptibility must depend upon the forces to which the wall is subject.

A plot of the energy of a ferromagnetic body as a function of position x of a given wall would be, over a small region, an irregular curve with many hills and valleys. When no field is present the wall will be found at a minimum position x_1. If the energy is assumed to be a continuous function of x, then near x_1,

$$V(x) = V(x_1) + (1/2\rho_r)(x-x_1)^2 + \cdots,$$

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[1] R. Gans, Z. Physik. **12**, 1053 (1911).
[2] R. S. Tebble and W. D. Corner, Proc. Phys. Soc. (London) **63**, 1005 (1950).
[3] Grimes, Orr, and Winsnes, Phys. Rev. **91**, 435 (1953).
[4] W. F. Brown, Jr., Phys. Rev. **52**, 325 (1937); Phys. Rev. **53**, 482 (1938); Phys. Rev. **54**, 279 (1938). These will be referred to as Parts I, II, and III, respectively.
[5] Rado, Wright, and Emerson, Phys. Rev. **80**, 273 (1950).