Correlations between normal-state properties and superconductivity

J. E. Hirsch
Department of Physics, University of California, San Diego, La Jolla, California 92093-0319
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Despite many years of intense theoretical effort it is still not possible to predict whether a material will be superconducting or not at low temperatures by measurement of its physical properties at higher temperatures. Nor is it possible in general to estimate the magnitude of the superconducting critical temperature T_c from measurements of normal-state properties. Here we address these questions from a statistical point of view. The metallic elements in the first six rows of the periodic table are assumed to be a ''representative sample'' drawn from a larger set of materials, and various statistical measures of correlations between the magnitude of T_c and a normal-state property, as well as between a normal-state property and the fact whether the material is or is not a superconductor, are considered. Thirteen normal-state physical properties are studied, some of which are believed to be important to determine superconducting properties within conventional BCS theory and others not. It is found that properties assumed to be important within BCS theory rank lowest in predictive power regarding whether a material is or is not a superconductor. Instead, properties with highest predictive power in this respect are found to be bulk modulus, work function and Hall coefficient. With respect to the magnitude of T_c, it is found to be positively correlated with electronic heat capacity, magnetic susceptibility, and atomic volume, and negatively correlated with electrical and thermal conductivity and Debye temperature. No significant correlations with ionic mass and ionization potential are found. Consequences of these findings for the theoretical understanding of superconductivity are discussed. [S0163-1829(97)01314-3]

I. INTRODUCTION

Why do some materials become superconducting when cooled, while others remain normal down to the lowest attainable temperatures? Why is the critical temperature very high in some superconducting materials and very low in others? Different theories suggest different explanations.[1–20] However, except for the fact that if a material becomes magnetic it is not likely to become superconducting, it has so far not been possible to predict the existence or nonexistence of superconductivity in a given material at low temperatures by observation of its properties at higher temperatures. Nor has it been possible in general to accurately predict the magnitude of the superconducting critical temperature T_c of a material from measurements of its normal-state physical properties.

There have been various attempts in the past to find empirical criteria relevant to these questions, some of which have met with some success.[21,22] Notable amongst these efforts was the criterion developed by Matthias, who uncovered a systematic variation of the superconducting T_c with the average number of valence electrons per atom.[23] Matthias empirical regularities have been verified in a large number of compounds (although exceptions have also been found[22,24]), but they have never been convincingly explained using the conventional BCS-electron-phonon framework.[1] It has also been claimed that theory alone,[25] or theory in combination with measurement of normal-state properties,[26] allows for calculation of the superconducting T_c; these calculations, however, have only been successfully applied to materials for which the critical temperature was known *before* it was calculated. The fact remains that superconductivity is found in an extraordinarily wide class of materials, and the question of which normal-state property or properties are most useful in yielding information on whether the material is superconducting or not, and on what the expected value of T_c is, is not well understood.

Furthermore, it is a fact that there are entire classes of new materials, such as high-T_c oxides and heavy fermion compounds, for which the conventional BCS-electron-phonon theory of superconductivity is generally believed not to be applicable. For other materials such as fullerenes, noncuprate oxides (BaKBiO, BaPbBiO), electron-doped oxides (NdCeCuO), and organic superconductors the applicability of the conventional theory is in doubt. It may be that the conventional theory of superconductivity will still be found to be applicable to these materials, or that there are one or more other mechanisms that apply to these as well as to materials that have not yet been discovered. It is also conceivable, albeit not believed likely, that one or more mechanisms other than the conventional one apply to ''conventional superconductors'' such as the elements; such a suggestion has been made in the past by Matthias.[27]

Faced with this situation, for the purposes of this paper we will assume we know nothing concerning the origin of superconductivity. That is, we imagine we are back in 1911 when superconductivity has just been discovered and no theory of it yet exists. The reason for doing so is to avoid being misled by any preconception that could conceivably be mistaken. We then address the questions stated in the first paragraph from a purely statistical point of view. Given the set of all possible materials, suppose one was able to draw a random sample of N materials such that any material in the population had equal probability of being selected. We may then analyze by statistical methods[28–30] correlations between various normal-state properties and superconductivity in the members of this sample. Such an analysis would allow us to test various possible hypothesis concerning the relationship between normal-state properties and superconductivity in the entire population, for example whether a given normal-state property is likely to be related or unrelated to superconductivity. Then one could make probabilistic predictions applicable to any new material concerning its superconductivity by measuring its normal-state properties, and focus the search for new superconductors on materials with certain normal-state properties and not others.

Unfortunately, we run into a serious difficulty right at the outset: how can we draw a random sample of all possible materials? The set of all *known* materials to date can hardly be assumed to be random with respect to all possible materials, since the materials that are not yet known are likely to be characterized by being on the average more difficult to synthesize, having a larger number of elements as components, etc. And even if we assumed the list of all known materials is an appropiate random sample, its size is so large that it would be very difficult to use it to carry out the analysis proposed in this paper.

For these reasons we will simplify our task and assume that the metallic elements in the first six rows of the periodic table are a random sample of the population of all possible materials. We do this for the practical reason that the size of this sample is not too large, and the physical properties of these elements have been throughly and accurately measured. Furthermore, since they exhibit a wide variety of electronic structures, crystal structures, as well as other physical properties, and they appear as components of most other materials, the assumption that they may be a ''random sample'' for the purposes of this paper may not be too farfetched. Alternatively, the reader not persuaded by these arguments may simply assume that the conclusions of this paper apply not to any material drawn at random from the set of all possible materials, but instead to any material drawn at random from the largest set of materials for which the set of elements we will use as our sample may be assumed to be a random sample.

We will consider thirteen normal-state properties in our analysis. The choice of these normal-state properties was guided by the criterion of making our task not too difficult: we started by choosing all the normal-state properties for which tables for the elements are given in Kittel's sixth edition.[31] We then eliminated the redundant ones, such as resistivity in favor of conductivity, atomic radii in favor of atomic volume, and cohesive energy which shows a strong correlation with melting temperature and bulk modulus (that were included). To keep this paper from getting too long we excluded also ionic radii and nuclear magnetic resonance data. We also included magnetic susceptibility (data not given in Kittel, but easily available). Of the resulting thirteen properties, some are suggested by the conventional theory of superconductivity to be important, e.g., Debye temperature (which contains information on phonon vibration frequencies), electronic specific heat (which contains information on electronic density of states), and electrical conductivity (which contains information on the strength of the electron-phonon interaction). Others are suggested to be important for superconductivity by other theories, or have been suggested to be important on empirical grounds in the past, while for others there is no *a priori* reason why they would be expected to be relevant to superconductivity, however, their possible relation to superconductivity has not been ruled out. When data on any of these properties for some of the elements were not contained in Kittel we used data of Refs. 32–34. The properties that we consider do not include the average number of valence electrons used by Matthias[23], so our results are complementary to his.

We consider two types of questions: (1) Is there any relation between a given normal-state property X and the existence or nonexistence of superconductivity in a material? In particular, do we increase the probability of correctly deciding whether the material is a superconductor or not by measuring property X? (2) For a superconducting material, is there any relation between the magnitude of T_c and the value of a normal-state property X? That is, do we increase our ability to estimate the value of T_c by measuring X? Finally, we would like to find out which of all the normal-state properties considered in this paper are most useful to give information on superconductivity, and what this implies with respect to the conventional as well as other theories of superconductivity.

The paper is organized as follows. In Sec. II we discuss the statistical procedures used. Section III, the bulk of the paper, gives results for various statistical measures of relationship between thirteen normal-state properties and superconductivity extracted from the elements. Section IV summarizes the main findings and analyzes their implications for various theories of superconductivity. In Sec. V we apply the same statistical procedures to a simple model system where the underlying probability distributions are known, to further support our analysis. We conclude in Sec. VI with a discussion.

II. STATISTICAL PROCEDURES

We will consider a sample set of $N=44$ elements, of which $N_1=25$ are found to be superconducting and $N_2=19$ nonsuperconducting. Let X be a normal-state property: we will study on one hand the distribution of X in superconducting (S) versus nonsuperconducting (N) materials and, on the other hand, possible correlations between the magnitudes of X and of the critical temperature.

A. Relation between a normal-state property and existence or nonexistence of superconductivity

For a given normal-state property X we can calculate its moments in our superconducting (S) and normal (N) samples. The mean and standard deviation are given by

$$\langle X\rangle_{S,N}=\frac{\Sigma_{i=1}^{N_j}X_i}{N_j}, \tag{1a}$$

$$\sigma_{S,N}=\sqrt{\sum_{i=1}^{N_j}\frac{(X_i-\langle X\rangle_{S,N})^2}{N_j}}, \tag{1b}$$

where the sums run over the sets of S or N elements in our sample. If one assumes a given form for the probability distributions, e.g., normal, there are simple tests to ascertain whether the observed differences in means are statistically significant, given the observed standard deviations. However, we will not make any assumption on the form of the underlying probability distributions. Thus it will be necessary to use nonparametric methods to compare the entire probability distributions, rather than summary measures such as mean and standard deviation. In fact we will find in some cases that these nonparametric methods can detect significant differences even when means and standard deviations are similar for both populations.

To obtain a frequency distribution for a normal-state property X in the sets S and N we will group the values of X into bins defining mutually exclusive classes. We will use (mostly) $n=5$ bins of equal size ranging from the lowest to the highest value of X observed. The reason for choosing $n=5$ is that it is small enough (given the number of elements in our sample) to allow for enough points in each bin for the statistical tests to be used to be approximately valid, and is large enough to preserve considerable detail in the distribution functions.

We define

$$P_{S,X}(X_i)=\text{probability that an } S \text{ material has } X=X_i, \tag{2a}$$

$$P_{N,X}(X_i)=\text{probability that an } N \text{ material has } X=X_i. \tag{2b}$$

The frequency distributions obtained from our samples represent our ''maximum likelihood estimators'' for the probability distributions defined by Eq. (2). Clearly, unless $P_{S,X}$ and $P_{N,X}$ are identical functions, measurement of the normal-state property X would provide some information on whether the material is likely to be superconducting or not.

More precisely, if we measure the property $X=X_i$ in a material we can calculate the probability that the material is a superconductor if the probabilities Eq. (2) are known using Bayes's theorem:

$$P(S/X_i)=\frac{P_{S,X}(X_i)P(S)}{P_{S,X}(X_i)P(S)+P_{N,X}(X_i)P(N)} \tag{3a}$$

and

$$P(N/X_i)=\frac{P_{N,X}(X_i)P(N)}{P_{S,X}(X_i)P(S)+P_{N,X}(X_i)P(N)}, \tag{3b}$$

where $P(S/X_i),P(N/X_i)$ are the probabilities that the material is superconducting or normal given that the value $X=X_i$ was measured for the normal-state property X. $P(S)$ and $P(N)$ are the *a priori* probabilities that the material is superconducting or normal respectively. Given our sample information the ''maximum likelihood'' estimators for these probabilities are

$$P(S)=\frac{25}{44}=0.57, \tag{4a}$$

$$P(N)=\frac{19}{44}=0.43. \tag{4b}$$

We will give below the maximum likelihood estimators for the conditional probabilities Eq. (3). First we would like to know, however, to what extent our sample information suggests that a normal-state property X is related to the existence or nonexistence of superconductivity in the material. We take as a null hypothesis,

$$H_0\text{: \textit{property X and existence of superconductivity are statistically independent}} \tag{5}$$

and test whether the sample information can rule out H_0 to some given level of significance α. The following tests will be used:[28,29]

1. Pearson χ^2 test of association

Let B_k, $1\leq k\leq n$ denote the bins (classes) for the normal-state property X defined above. Let A_j, $j=1,2$, denote the classes of S and N materials in our sample. We count the number of elements of class A_j in bin B_k and denote it by f_{jk}:

$$f_{jk}=\text{observed frequency of class } A_j \text{ in category } B_k. \tag{6}$$

Let $N=N_1+N_2$ be the total number of elements in our sample. Then the estimated probability that an element in class A_j has normal-state property in bin B_k is

$$P_{\text{est}}(A_j,B_k)=\frac{f_{jk}}{N}. \tag{7}$$

The estimated probability for an element to be in class A_j is

$$P_{\text{est}}(A_j)=\frac{N_j}{N} \tag{8}$$

and the observed frequency in bin B_k for both classes (S and N) is

$$f_k=\sum_{j=1,2} f_{jk} \tag{9}$$

so that the estimated probability for bin B_k is

$$P_{\text{est}}(B_k)=\frac{f_k}{N}. \tag{10}$$

If the attributes A and B were independent, we would expect the approximate equality in our sample

$$P_{\text{est}}(A_j,B_k)\sim P_{\text{est}}(A_j)P_{\text{est}}(B_k) \tag{11}$$

and large differences between the two sides of this equation would suggest nonindependence. We calculate the quantity

$$\chi^2=\sum_{j,k}\frac{(f_{jk}-f_{e,jk})^2}{f_{e,jk}}, \tag{12}$$

where

$$f_{e,jk}=NP_{\text{est}}(A_j)P_{\text{est}}(B_k) \tag{13}$$

is the estimated frequency of class A_j in category B_k assuming independence. The variable χ^2 so defined is distributed according to χ^2 statistics with $(n-1)$ degrees of freedom ($n=$ number of categories B_k).[28]

In other words, suppose we decide that we will reject the null hypothesis of independence if our sample has probability less than $\alpha=0.05$ under that hypothesis. We compute χ^2 from Eq. (12) above, find the probability of such a value of χ^2 for a χ^2 distribution with $n-1$ degrees of freedom, $P_{n-1}(\chi^2)$, and reject the hypothesis of independence if

$$P_{n-1}(\chi^2)<\alpha. \tag{14}$$

For example, for $\alpha=0.05$, $n=5$, we find from statistical tables that the equality in Eq. (14) holds for $\chi^2=9.49$. Thus, if the value of χ^2 for our sample is found to be larger than 9.49 we conclude that a relationship does exist between that normal-state property and existence of superconductivity at the 0.05 level of significance.

A quantitative measure of the strength of the relationship between categories A and B is given by the index φ:

$$\varphi=\sqrt{\frac{\chi^2}{N}} \tag{15}$$

(N=total number of elements in the sample), which ranges from 0, indicating complete independence, to 1, indicating complete association. For our case, $\varphi=1$ corresponds to the case where all the members in any given bin of normal-state property X are either S or N. The index φ is somewhat analogous to the ordinary correlation coefficient between two statistical variables.

2. Kolmogoroff-Smirnoff test of association

This test has the advantage that it does not require grouping of the X values into bins. We simply compute the cumulative frequency distributions $F_S(X)$ and $F_N(X)$ for the superconducting and normal elements in the sample. The test involves the maximum difference in these functions,

$$D=\max_X|F_S(X)-F_N(X)|. \tag{16}$$

The distribution function for D can be obtained from statistical tables[29] or asymptotically from the expression

$$P\left[D>z\left(\frac{1}{N_1}+\frac{1}{N_2}\right)^{1/2}\right]=2e^{-2z^2} \tag{17}$$

so the hypothesis of independence is rejected at the α level of significance for

$$D>\sqrt{-\frac{1}{2}\ln\frac{\alpha}{2}\left(\frac{1}{N_1}+\frac{1}{N_2}\right)} \tag{18}$$

or, for given D, the corresponding α is

$$\alpha=2e^{-2z^2} \tag{19a}$$

with

$$z=\frac{D}{[(1/N_1)+(1/N_2)]^{1/2}}. \tag{19b}$$

3. Measures of predictive association

How can we decide whether a material is likely to be S or N? In the absence of any information on its normal-state property X, we would necessarily decide it is S, according to the principle of maximum likelihood given our sample, since from Eq. (4)

$$P(S)>P(N). \tag{20}$$

The probability of error in this decision would be

$$P(\text{error})=1-P(S). \tag{21}$$

Now if S and N materials have different probability distributions for the normal-state property X, we can increase our ability to decide this question, i.e., reduce the probability of error, if we know the conditional probabilities Eq. (3). For the measured value $X=X_i$ we would conclude that the material is likely to be superconducting if

$$P(S/X_i)>P(N/X_i) \tag{22a}$$

and conversely that it is likely to be normal if

$$P(N/X_i)>P(S/X_i). \tag{22b}$$

It is easy to see that the probability of error is in general reduced by measuring X. Let A_j denote the classes S, N for $j=1,2$, and B_k the possible value ranges for X, as in the previous subsection. We have

$$P(\text{error}/X\ \text{unknown})=1-\max_j P(A_j), \tag{23a}$$

$$P(\text{error}/X\in B_k)=1-\max_j P(A_j/B_k). \tag{23b}$$

Furthermore

$$P(A_j/B_k)=\frac{P(B_k/A_j)P(A_j)}{P(B_k)} \tag{24}$$

and

$$\begin{aligned}P(\text{error}/X\ \text{known})&=\sum_k P(\text{error}/X\in B_k)P(B_k)\\&=1-\sum_k \max_j P(B_k/A_j)P(A_j)\end{aligned} \tag{25}$$

so that

$$\begin{aligned}&P(\text{error}/X\ \text{unknown})-P(\text{error}/X\ \text{known})\\&=\sum_k \max_j P(B_k/A_j)P(A_j)-\max_j P(A_j).\end{aligned} \tag{26}$$

Since

$$\sum_k P(B_k/A_j)P(A_j)=P(A_j) \tag{27}$$

Eq. (26) is zero if $\max_j P(B_k/A_j)$ is independent of k, and larger than zero otherwise. The overall effectiveness of the property X in reducing the error can be quantified with the "index of predictive association"[28]

$$\lambda=\frac{P(\text{error}/X\ \text{unknown})-P(\text{error}/X\ \text{known})}{P(\text{error}/X\ \text{unknown})} \tag{28}$$

and ranges between 0 and 1.

We can estimate these probabilities in terms of the measured frequencies f_{jk} [Eq. (6)] for our sample of N elements:

$$P(A_j)=\sum_k \frac{f_{jk}}{N}\equiv\frac{f_j}{N}, \tag{29a}$$

$$P(B_k)=\sum_j \frac{f_{jk}}{N}\equiv\frac{f_k}{N}, \tag{29b}$$

$$P(B_k/A_j)=\frac{f_{jk}}{f_j}, \tag{29c}$$

$$P(A_j/B_k)=\frac{f_{jk}}{f_k}. \tag{29d}$$

The probabilities of error are

$$P(\text{error}/X\ \ \text{unknown})=1-\frac{\max_j f_j}{N}, \tag{30a}$$

$$P(\text{error}/X\ \ \text{known})=1-\frac{1}{N}\sum_k\ \max_j f_{jk} \tag{30b}$$

and the index of predictive association Eq. (28) is estimated as

$$\lambda=\frac{\Sigma_k \max_j f_{jk}-\max_j f_j}{N-\max_j f_j}. \tag{31}$$

B. Relation between a normal-state property and the magnitude of T_c

In this subsection we consider only the superconducting elements in our sample, and redefine N to be the number of such elements ($N=25$). We would like to know whether a relationship between the value of a normal-state property X for a given superconducting material and the magnitude of its T_c exists. We will consider several different measures of relationship in our sample. Our null hypothesis again is

H_0: *property X and the magnitude of T_c are statistically independent* (32)

and we will test whether the sample information can rule out H_0 to some given level of significance α. We denote by X_i the value of normal-state property X for a given element, and Y_i its value of T_c. The following measures will be considered.

1. Correlation coefficient

The simplest way to measure a relationship between X and Y is through the correlation coefficient. An estimator of the correlation coefficient over our sample is

$$r=\sum_{i=1}^{N}\frac{(X_i-\langle X\rangle)(Y_i-\langle Y\rangle)}{\sigma_X\sigma_Y}, \tag{33}$$

where the sum is over the superconducting elements in the sample, and averages and standard deviations are defined as in Eq. (1). The values of r range between -1 and 1, with $r=0$ indicating no correlation and $|r|=1$ perfect correlation.

The null hypothesis that the correlation coefficient estimated from our sample is a random deviation from zero correlation in the population is tested by the t distribution with $N-2$ degrees of freedom,[29] with

$$t=|r|\sqrt{\frac{N-2}{1-r^2}}. \tag{34}$$

Tables of the t distribution are found in most textbooks on statistics.

Strictly speaking the correlation coefficient measures the degree of *linear* relationship between X and Y, so that if the variables are related in a nonlinear fashion it would result in $|r|<1$. In the following we consider more general tests of correlations that can detect more qualitative monotonic trends.

2. Spearman rank correlation coefficient

The values of X and Y are ordered monotonically and assigned an increasing rank to each successive value, starting at 1. Let D_i be the difference in the ranks of X_i and Y_i associated with the particular element i. The Spearman rank correlation coefficient is given by[29]

$$r_S=1-\frac{6\Sigma_i D_i^2}{N(N^2-1)}. \tag{35}$$

Just as the ordinary correlation coefficient, r_S ranges between -1 and 1, with small values of $|r_S|$ suggesting no correlation. Contrary to r, r_S will take the values 1 or -1 even if the relation between X and Y is nonlinear, provided it is monotonic. The hypothesis of independence at significance level α can be tested by looking up standard tables for the Spearman rank correlation coefficient with N degrees of freedom, or by the t distribution with $N-2$ degrees of freedom, with

$$t=|r_S|\sqrt{\frac{N-2}{1-r_S^2}} \tag{36}$$

for N large ($N\geqslant 30$).

3. Kendall τ coefficient

This correlation coefficient measures the qualitative tendency to a monotonic relationship between X and Y by counting the number of inversions in orders of pairs. An inversion exists for elements i and j if $X_i>X_j$ and $Y_i<Y_j$, or vice versa. The τ coefficient is defined as[28]

$$\tau=1-\frac{2(\text{number of inversions})}{\text{number of pairs of objects}}. \tag{37}$$

τ also ranges between -1 and 1, and its interpretation is as follows: if two objects are drawn at random, the probability that they show the same relative order in variables X and Y is τ more than the probability that they show opposite order. If the variables X and Y are statistically independent the distribution of τ approaches rapidly a normal distribution as N increases, with mean zero and variance

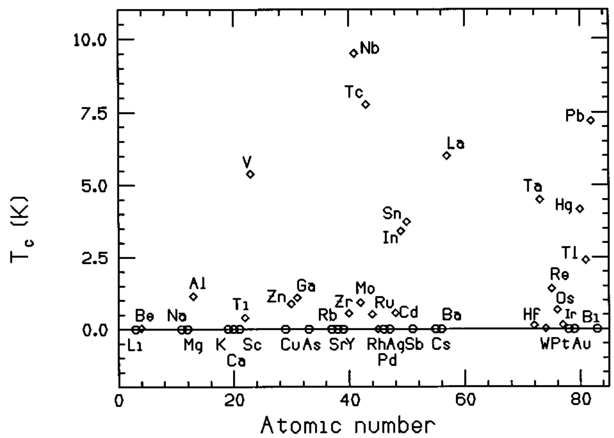

FIG. 1. Superconducting T_c versus atomic number for elements in our sample. In this and the following figures, data for superconducting elements are indicated by diamonds and those for nonsuperconducting elements by circles.

$$\sigma_\tau^2=\frac{2(2N+5)}{9N(N-1)}. \tag{38}$$

Thus the null hypothesis of statistical independence is tested (for $N\geqslant 10$) by constructing the normalized variable

$$z=\frac{\tau}{\sigma_\tau} \tag{39}$$

and checking whether the sample value obtained for z is compatible with it being a normally distributed random variable with mean 0 and standard deviation 1 to a given level of significance α.

III. RESULTS

Our sample consists of 44 elements ranging from Lithium (atomic number 3) to Bismuth (atomic number 83). It includes all the metallic and semimetallic elements in the first six rows of the periodic table, except for the magnetic elements Cr, Mn, Fe, Co, Ni, and the lanthanides (atomic number 58 to 71), which also exhibit magnetic properties. The magnetic elements are excluded because magnetism is known to exclude superconductivity in almost all known materials, hence we exclude magnetic materials from our general population also. The semimetals As, Sb, and Bi are included, even though they are all nonsuperconductors under normal conditions, because there is no *a priori* reason why they couldn't be superconductors; there are other materials with similar physical properties (e.g., low carrier concentration, high resistivity) that are in fact superconducting, and in fact these elements do become superconducting under pressure.

In this sample, 25 elements are found to be superconducting, with transition temperatures ranging from 9.5 K (Nb) down to 0.3 mK (Rh). The average T_c is $\langle T_c\rangle=2.45$, and its standard deviation $\sigma_{T_c}=2.74$. The remaining 19 elements in our sample are nonsuperconductors down to the lowest temperature studied. Figure 1 shows T_c plotted versus atomic number for the elements considered.

We have considered thirteen normal-state properties. Numerical values for these properties were obtained from Refs. 31–34. Table I lists these properties, and their average values and standard deviations over all elements considered as well as over the superconducting and nonsuperconducting elements separately. There are some clear differences in the averages, for example nonsuperconductors are better conductors of electricity and heat in the normal state, their melting temperatures are lower, they have larger atomic volumes and are more compressible. However, in all cases one or both standard deviations are larger than the difference in average values, so that these differences cannot be assumed to be significant without further test.

Table I also lists the correlation coefficient [Eq. (33)] between T_c and each normal-state property, for all elements in the sample. Here we do not differentiate between superconductors and nonsuperconductors, i.e., we allow for the possibility that materials now believed to be nonsuperconductors will be found in the future to have a small nonzero T_c. It can be seen that the correlation coefficient so computed is never very large. Except for the one corresponding to heat capacity (0.34), none of these correlation coefficients is significant at the 5% level ($r_{XY}=0.34$ is significant at the 2.4% level for $N=44$). Below we will compute these and other correlation coefficients for superconducting members of the sample only.

We now consider each normal-state property in detail. For each property, we show a scatter plot of T_c versus the normal-state property (X), that gives a qualitative picture of the distribution. Then we group the X values into bins of equal size and plot the frequency distribution of X for superconductors and nonsuperconductors in the sample. We plot the midpoints of each interval and connect the points by smooth lines; equivalent information would be contained in a histogram. We show also the cumulative distributions and their maximum difference, which is the quantity used in the Kolmogorff-Smirnoff test. Finally, we plot the conditional probabilities infered from our data for a material to be or not to be a superconductor given the value of its normal-state property X [Eq. (3)]. In Tables II and III we summarize the results for the various statistical quantities computed.

A. Ionic mass

Both the lightest (Li, $M=6.9$) and heaviest (Bi, $M=209$) elements in our sample are non-superconductors; however, the elements next to them are both superconductors (Be, $M=9.0$ and Pb, $M=207$), and both superconductors and nonsuperconductors are distributed fairly uniformly in that range, as seen in Fig. 2. BCS theory suggests that everything else being equal T_c should vary inversely with the square root of the ionic mass. However, such a trend is clearly not evident in Fig. 2. The cumulative probability distributions show maximum deviation of $D=0.339$, which implies that the hypothesis that ionic mass is independent of whether a material is superconducting or not can only be rejected at the $\alpha=0.17$ level of significance. $\chi^2=5.91$ similarly implies that H_0 is rejected at the $\alpha=0.20$ level of significance. Hence we conclude that our sample is consistent with ionic mass being independent of existence of superconductivity at the 5% level (in other words, more than 5% of samples of superconductors and nonsuperconductors would look as dif-

TABLE I. Average values and standard deviations of normal-state properties over superconducting (S) (25 elements, 23 for Hall coefficient) and nonsuperconducting (N) (19 elements, 17 for Hall coefficient) elements in the sample separately (first 4 columns) as well as over the entire sample (columns 5 and 6). Column 7 gives the correlation coefficient between T_c and the normal-state property over the entire sample.

Property (X)	$\langle X\rangle_S$	σ_S	$\langle X\rangle_N$	σ_N	$\langle X\rangle$	σ	r_{XY}
Ionic mass (mass number)	122.5	58.9	94.0	58.8	110.2	60.5	0.19
Heat capacity (γ in mJ mol^{-1} K^{-2})	3.11	2.56	3.19	3.37	3.15	2.94	0.34
Electrical conductivity [$10^5(\Omega-\mathrm{cm})^{-1}$]	1.12	0.89	1.65	1.87	1.35	1.42	-0.27
Debye temperature (K)	357	262	214	104	295	220	-0.15
Ionization potential (eV)	7.49	1.22	6.74	1.75	7.17	1.52	-0.027
Effective U (eV)	9.10	2.23	16.1	15.7	12.1	11.0	-0.20
Work function (eV)	4.45	0.44	3.62	1.11	4.09	0.90	0.13
Bulk modulus (10^{12} dyn/cm^2)	1.64	1.24	0.61	0.75	1.19	1.17	0.088
Melting temperature (K)	1831	1109	1043	547	1490	990	0.12
Atomic volume (Å^3)	19.6	7.0	38.7	26.6	27.9	20.6	-0.15
Thermal conductivity (W cm^{-1} K^{-1})	0.827	0.61	1.18	1.27	0.979	0.966	-0.29
Magnetic susceptibility (10^{-6} cm^3/mol)	60.1	91.4	47.1	166	54.4	129	0.21
Hall coefficient ($1/R_H$ in 10^{11} Å sec/m^3)	0.0622	0.142	-0.100	0.11	-0.068	0.15	0.22

ferent or more from each other as ours if those quantities are independent). The conditional probabilities in Fig. 2 show that knowing the value of ionic mass does not help much in deciding whether a system is or is not superconducting, and the overall index of predictive association is a low $\lambda=0.26$.

Our tests of correlation between ionic mass and magnitude of T_c (Table III) show a small *positive* correlation in all the tests considered. This is contrary to the expectation of BCS theory. However, the α coefficients are all very large, indicating that our data are consistent with magnitude of T_c and ionic mass being statistically independent.

B. Electronic specific heat

Figure 3 shows results for the electronic heat capacity constant γ. Since it is expected to be directly proportional to the electronic density of states at the Fermi level, BCS as well as other theories suggest that superconductivity and in particular high T_c should be associated with large values of γ. Indeed we see that the lowest values of γ occur in nonsuperconductors (the semimetals). However, the highest values of γ also correspond to nonsuperconductors, Sc and Y. Both the frequency distributions and cumulative distributions are very similar for superconductors and nonsuperconductors. The value of χ^2 and of the Kolmogoroff-Smirnoff coefficient D are very low, 2.22 and 0.19 respectively, indicating that the sample information is consistent with superconductors and nonsuperconductors having the same probability distribution for γ. The index of predictive association, $\lambda=0.053$, is the lowest of all properties considered.

The conditional probability graph appears to suggest that for values of $\gamma\sim 5$ mJ/mol K^2 superconductivity is strongly favored. However, there are only two superconductors (and no nonsuperconductors) in this bin (γ between 4.3 and 6.4) in our sample; assuming the actual probability for a material to have a γ in this range is as given by the superconducting sample, $p=2/25=0.08$ (sample size is $N_1=25$), the expected value for the number of nonsuperconductors in this range for sample size $N_2=19$ is 1.5, and the probability of a fluctuation where there are no nonsuperconductors in this range in a sample of this size is $(1-p)^{19}=21\%$, i.e., rather high.

While there seems to be no correlation between existence of superconductivity and γ, there is indeed a substantial correlation between the magnitude of T_c and the electronic specific-heat coefficient, as seen in Table III. In particular the correlation coefficient $r=0.61$ is the largest of all properties considered, which for a sample of this size is due to pure chance with probability $\alpha=0.11\%$. Even though the other tests yield larger values of α, it is reasonable to take the

TABLE II. Statistical measures of association between normal state properties and superconductivity. First two columns give the value of χ^2 [Eq. (12)] and the associated probability α assuming statistical independence between the normal state property and existence of superconductivity [Eq. (14) with equal sign], for the observations divided into five bins of equal size (four bins for Hall coefficient). Third column is the index φ, Eq. (15), fourth and fifth columns the Kolmogoroff-Smirnoff index D [Eq. (16)] and its associated probability, and sixth column the index of predictive association Eqs. (28), (31). Test case properties X and Y are discussed in Sec. V.

Property	χ^2	α_{χ^2}	φ	D	α_D	λ
Ionic mass	5.91	0.20	0.37	0.339	0.17	0.26
Heat capacity	2.22	>0.5	0.23	0.194	>0.5	0.053
Electrical conductivity	4.78	0.31	0.33	0.236	>0.5	0.16
Debye temperature	7.88	0.096	0.43	0.389	0.076	0.21
Ionization potential	6.08	0.19	0.37	0.328	0.20	0.21
Effective U	7.42	0.11	0.41	0.352	0.14	0.26
Work function	16.9	0.0020	0.62	0.592	0.0011	0.53
Bulk modulus	8.09	0.088	0.43	0.564	0.0020	0.26
Melting temperature	12.70	0.013	0.54	0.520	0.0058	0.32
Atomic volume	9.27	0.055	0.46	0.406	0.057	0.32
Thermal conductivity	4.78	0.31	0.33	0.171	>0.5	0.16
Magnetic susceptibility	7.02	0.13	0.40	0.309	0.25	0.16
Hall coefficient	20.7	0.00013	0.72	0.783	1.3×10^{-5}	0.65
Test case property X	17.8	0.0014	0.64	0.587	0.0012	0.42
Test case property Y	6.37	0.17	0.38	0.322	0.21	0.26

lowest α value as significant, hence we conclude that the magnitude of T_c is indeed positively correlated with γ, as predicted by BCS and other theories.

C. Electrical conductivity

Room temperature values of electrical conductivity were used. The largest electrical conductivities are found for the nonsuperconducting elements Cu, Ag, and Au ($\sigma=5.88,6.21,4.55\times10^5\ \Omega\ \mathrm{cm}^{-1}$) (Fig. 4). On the other hand, the lowest conductivity in our sample is also found in a non-superconductor (Bi, with $\sigma=0.086\times10^5\ \Omega\ \mathrm{cm}^{-1}$). The frequency distributions and cumulative distributions are similar, with superconductors predominating at low conductivity and nonsuperconductors at high conductivities. The conditional probabilities suggest much higher probabilities for nonsuperconductors at high conductivities, however, because the number of sample elements is small in this region this is not very significant. The values of χ^2 and D are rather low, 4.78 and 0.24, yielding values of α of 0.31 and >0.5.

TABLE III. Statistical measures of correlation between T_c and normal-state properties in superconducting sample. Column 1 gives the values of the ordinary correlation coefficient Eq. (33), column 2 the Spearman rank correlation coefficient Eq. (35), and column 3 the Kendall τ coefficient Eq. (37). Columns 4 to 6 give the associated probabilities for these coefficients for a sample of this size assuming statistical independence between the normal state property and T_c.

Property	r	r_S	τ	α_r	α_{r_S}	α_τ
Ionic mass	0.110	0.148	0.107	>0.5	0.48	0.45
Heat capacity	0.613	0.358	0.240	0.0011	0.078	0.093
Electrical conductivity	−0.442	−0.453	−0.333	0.027	0.024	0.019
Debye temperature	−0.404	−0.565	−0.380	0.045	0.0032	0.0078
Ionization potential	−0.246	−0.355	−0.240	0.23	0.082	0.093
Effective U	−0.263	−0.336	−0.227	0.20	0.10	0.11
Work function	−0.321	−0.311	−0.213	0.12	0.13	0.14
Bulk modulus	−0.197	−0.297	−0.213	0.34	0.15	0.13
Melting temperature	−0.119	−0.235	−0.160	0.59	0.25	0.26
Atomic volume	0.375	0.438	0.307	0.064	0.029	0.032
Thermal conductivity	−0.473	−0.459	−0.333	0.017	0.022	0.019
Magnetic susceptibility	0.407	0.083	0.020	0.043	>0.5	>0.5
Hall coefficient	−0.071	−0.102	0.0672	>0.5	>0.5	>0.5
Test case property X	0.222	0.168	0.118	0.28	0.41	0.43
Test case property Y	0.614	0.598	0.433	0.0011	0.0020	0.0024

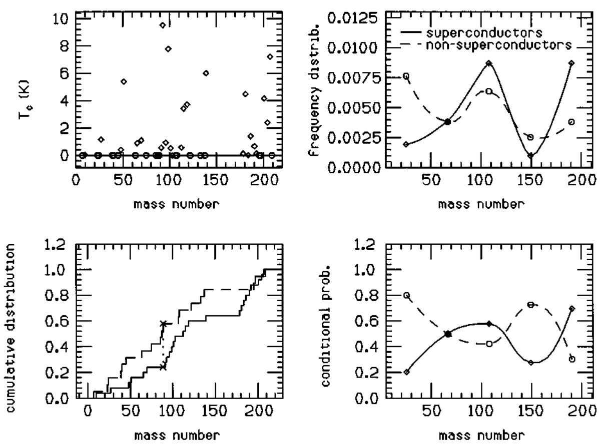

FIG. 2. In this and the following twelve figures: upper left shows scatter plot of T_c versus normal-state property. Upper right gives the frequency distributions for superconductors and nonsuperconductors divided into five bins (four for Hall coefficient) of equal size; the points correspond to the center of the bin, the lines are drawn smoothly between points to guide the eye. Lower right gives the conditional probability distributions for a material being superconducting (solid line) or nonsuperconducting given a value of the normal-state property, from Eqs. (3) and (29d). Lower left gives the cumulative probability distributions for superconductors (solid line) and nonsuperconductors (dashed line); the maximum difference (used in the Kolmogoroff-Smirnoff test) is indicated by a dotted line connecting crosses. In this figure, the normal-state property is the mass number.

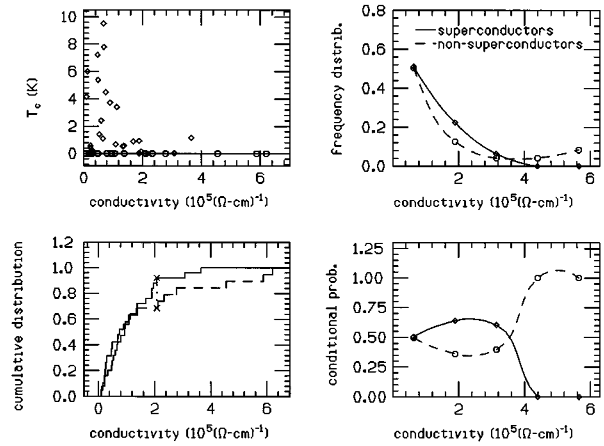

FIG. 4. Same as Fig. 2 for electrical conductivity in units $10^5(\Omega-\text{cm})^{-1}$.

Thus our sample is consistent with the same probability distributions for conductivities in superconducting and nonsuperconducting materials. The index of predictive association is also low, $\lambda=0.16$. This appears to be at odds with the expectation based on BCS theory that superconductivity should be associated with large values of the electron-phonon coupling constant which should also lead to high resistivities.

On the other hand, the scatter plot does suggest a negative correlation between magnitude of T_c and conductivity in superconductors, and the statistical tests in Table III confirm this: all three tests indicate that the hypothesis of independence of magnitude of T_c and electrical conductivity should be rejected at a level of significance $\alpha=2.7\%$ or smaller. The value of the Kendall τ coefficient indicates that if a given material has a larger conductivity than another, the probability that it has also a smaller T_c than the other is 33% higher than the converse. These results are qualitatively consistent with the BCS expectation that higher T_c's should be associated with larger resistivities.

D. Debye temperature

The elements with lowest Debye temperatures in our sample (Cs,Rb) are nonsuperconductors, while those with the highest θ_D (Be,Ru) are. More generally, Fig. 5 shows that nonsuperconductors tend to have lower values of θ_D than superconductors. Because Be ($\theta_D=1440$ K) has a value of Θ_D so much higher than all other elements (5 σ's higher than the mean) we have excluded it in the calculation of the frequency distributions in Fig. 5. The conditional probabilities suggest that materials with low θ_D ($\theta_D\leqslant 350$ K) are somewhat more likely to be nonsuperconductors, while those with high θ_D are much more likely to be superconductors.

The values of χ^2 and D are found to be 7.88 and 0.39 respectively, yielding α values of 0.096 and 0.076 respectively. Thus at the 10% level we would reject the hypothesis that existence of superconductivity and θ_D are unrelated; in

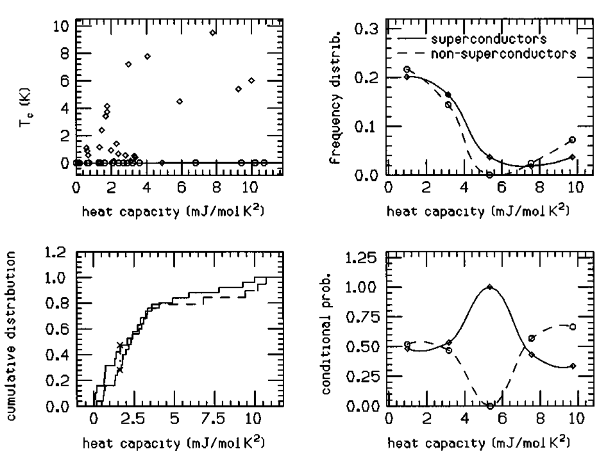

FIG. 3. Same as Fig. 2 for the electronic specific-heat coefficient γ in units mJ/mol/K^2.

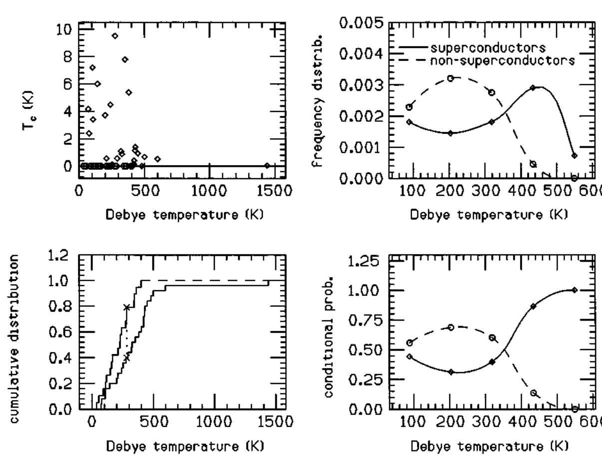

FIG. 5. Same as Fig. 2 for Debye temperature in units of K.

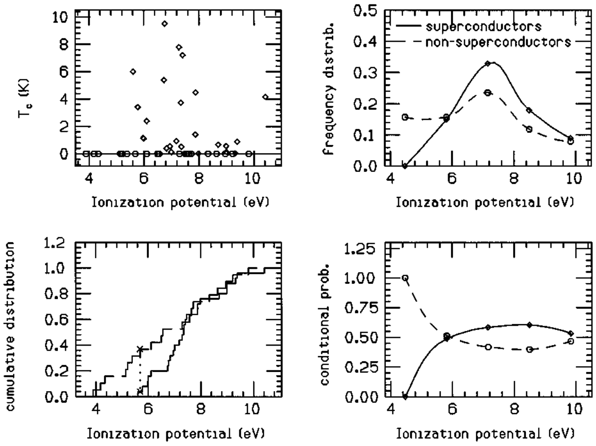

FIG. 6. Same as Fig. 2 for ionization potential in eV.

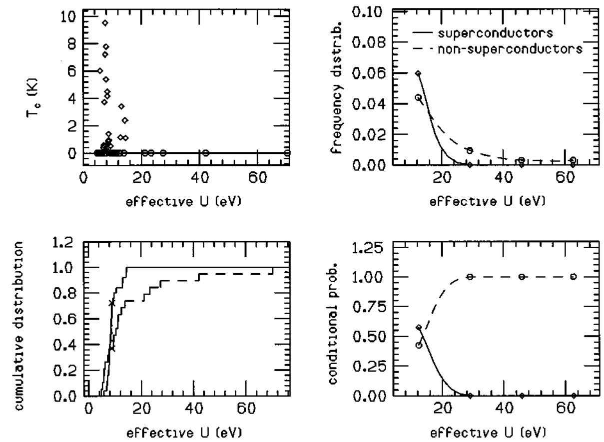

FIG. 7. Same as Fig. 2 for effective U, defined as the difference between second and first ionization potentials, in eV.

other words, there is less than a 10% chance that our samples of superconducting and nonsuperconducting elements would come from a populations with the same distribution of θ_D's. However at the 5% level the results are consistent with statistical independence of θ_D and existence of superconductivity. The index of predictive association is still rather low, $\lambda = 0.21$.

On the other hand, there appears to be a definite *negative* correlation between magnitude of T_c and Debye temperature, as Table III shows. In particular the Spearman r_S coefficient indicates that the probability of no correlation between these quantities is less than 0.3%, thus we reject the hypothesis of independence. Even though θ_D appears as a prefactor of T_c within BCS theory, the fact that high T_c's can result from low θ_D's has been explained in the past as due to the fact that the electron-phonon coupling is larger for materials with low θ_D.

E. Ionization potential

The six lowest ionization potentials are found in nonsuperconducting elements, the alkali and alkali-earth metals. The highest ionization potential corresponds to a superconducting element, Hg. Except for this preponderance of nonsuperconductors at low ionization potential (E_I) the probability distributions are rather similar, as seen in Fig. 6. The conditional probabilities suggest that materials with low ionization potential are much more likely to be nonsuperconductors, while for high ionization potential the probabilities for superconductors and nonsuperconductors are almost equal. Because there is a substantial number of members of our sample in the low-ionization potential region this distinction is significant.

On the other hand, the global measures of statistical independence χ^2 and D for our sample yield the values 6.08 and 0.33 respectively, corresponding to values of α of 0.19 and 0.20. These are consistent with ionization potential and existence of superconductivity being statistically independent. The index of predictive association also yields a low value, $\lambda = 0.21$. Therefore, our sample suggests that except for the lowest values of E_I there is no correlation between ionization potential and superconductivity.

Concerning the magnitude of T_c the situation is reversed: Table III shows a small negative correlation between T_c and ionization potential, i.e., small ionization potential tends to favor higher T_c's. However the correlation found is not significant at the 5% level in any of the tests considered.

F. Second ionization potential (effective U)

Instead of considering the second ionization potential E_II directly, we have instead considered the ''effective U'' defined as the difference between second and first ionization potentials,

$$U_\mathrm{eff} = E_\mathrm{II} - E_\mathrm{I}. \tag{40}$$

U_eff represents the effective repulsion for two electrons added to the doubly ionized atom, and one may expect that a low value of U_eff could be favorable to superconductivity, as has been suggested theoretically.[5,35] In fact, the five largest effective U's correspond to nonsuperconductors, the alkali atoms, resulting from the combination of a low first ionization potential and a high second ionization potential. However, the two lowest values of U_eff are also found in nonsuperconductors, the alkali earths Ba and Sr. The range of variation in U_eff is found to be substantially smaller in superconductors than in nonsuperconductors, as seen in Table I, and the conditional probabilities in Fig. 7 suggest that a material with a large value of U_eff is more likely to be a nonsuperconductor. However, the global measures of statistical independence χ^2 and D yield values 7.42 and 0.35, corresponding to α values of 0.06 and 0.14, so the differences in U_eff found in our sample for superconductors and nonsuperconductors are not significant at the 5% level. The index of predictive association is also rather low, 0.26.

Concerning the magnitude of T_c, we find some indication of a negative correlation as one would expect, i.e., higher T_c's associated with lower values of U_eff. However, none of the correlation measures considered are found significant at the 5% level as seen in Table III.

G. Work function

Values of the work function are expected to be related to ionization potentials, and indeed we find a correlation coefficient $\rho = 0.78$ beween the two quantities in the sample considered. Nevertheless, correlations with superconductivity

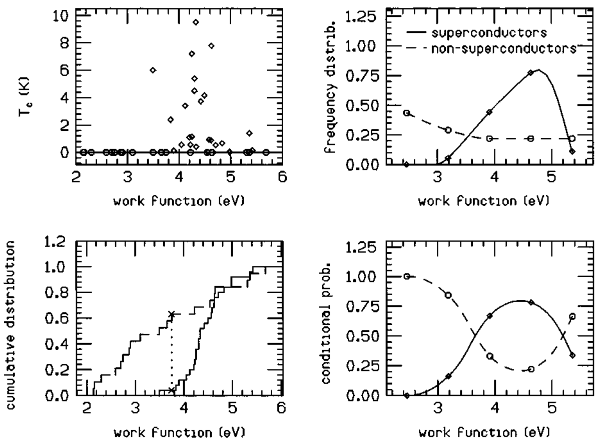

FIG. 8. Same as Fig. 2 for work function in eV.

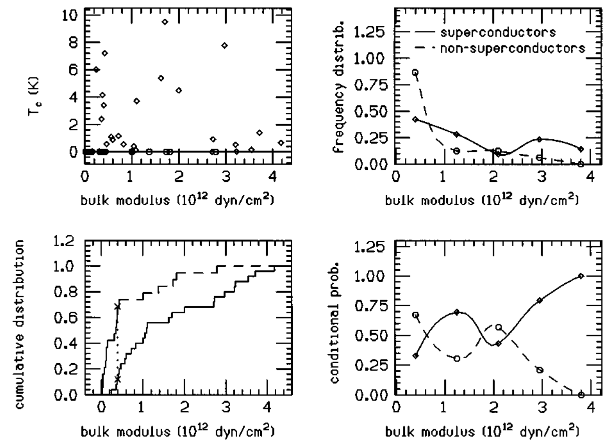

FIG. 9. Same as Fig. 2 for bulk modulus in units 10^{12} dyn/cm^2.

are found to be substantially larger for work functions. In fact, Koshida[36] has suggested in the past the existence of an empirical relation between work fuction and superconductivity.

The nine lowest work functions are found in nonsuperconducting elements (as opposed to only the six lowest ionization potentials), leading to a rather large value of the Kolmogoroff-Smirnoff coefficient $D=0.59$. This indicates that the probability that work functions in S and N are governed by the same distribution is about 0.1%. The value of χ^2 is also large ($\chi^2=16.9$), as is the index of predictive association $\lambda=0.53$. In other words, knowing the value of the work function reduces the probability of error in predicting whether a material is superconducting or not by over 50%. The probability distributions in Fig. 8 show that materials with intermediate values of the work function (4 to 5 eV) are most likely to be superconductors, and those with higher and lower work functions are most likely nonsuperconductors.

On the other hand, the results in Table III suggest that there is a negative correlation between magnitude of T_c and work function. However, the correlation is found to be not significant at the 10% level.

H. Bulk modulus

Do superconductors tend to be hard or soft? There are of both kinds according to the distributions in Fig. 9, e.g., Hg and Pb are quite soft (bulk moduli 0.38 and 0.43×10^{12} dyn/cm^2) while Re and Os are quite hard (bulk moduli 3.78 and 4.2×10^{12}dyn/cm^2). However, the overall tendency is for superconducting elements to be harder than nonsuperconducting ones. The eight lowest values of bulk moduli correspond to nonsuperconductors (alkalis and alkali earths) and the six highest to superconductors (transition metals). Thus there is a definite difference in the distribution of bulk moduli of superconductors and nonsuperconductors in our sample. This is most clearly detected by the Kolmogoroff-Smirnoff D coefficient of 0.56, which yields a value of $\alpha=0.0020$. That is, the probability that bulk moduli in S and N are governed by the same distribution is less than 0.2%. The frequency distributions and conditional probabilities show that low values of bulk modulus (high compressibility) indicates that a material is likely to be nonsuperconducting, and high values (low compressibility) that it is superconducting. Nevertheless the index of predictive association $\lambda=0.26$ is not very high.

The situation is again reversed concerning the magnitude of T_c, as the results of Table III suggest that high T_c's are associated with low values of the bulk modulus, i.e., high compressibilities. However, the hypothesis of independence of T_c and bulk modulus cannot be rejected even at the 10% level of significance from our sample data.

I. Melting temperature

Matthias suggested that there may be a connection between superconductivity and melting temperatures, namely that high T_c's should be associated with low melting points.[37] The data in Fig. 10 show that the range of T_M's seen in superconducting elements is considerably wider than in nonsuperconducting ones, e.g., both the lowest (Hg, $T_M=234.3$ K) and highest (W, $T_M=3695$ K) melting temperatures correspond to superconducting elements. The probability distributions in Fig. 10 indicate that high T_M's yield a higher probability of being superconducting, while low T_M's indicate higher probability for the system being normal. The index of predictive association $\lambda=0.32$ is the highest of all properties considered so far except for work function.

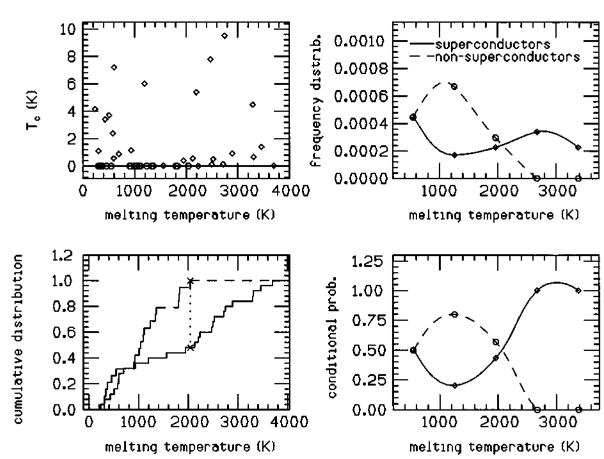

FIG. 10. Same as Fig. 2 for melting temperature in K.

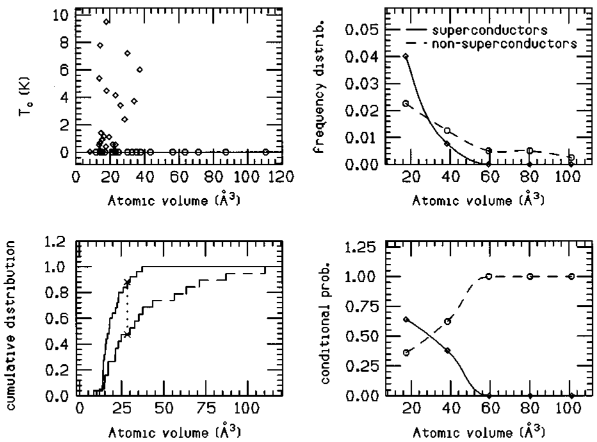

FIG. 11. Same as Fig. 2 for atomic volume in Å^3.

The data indicate a strong probability that melting temperature distributions for superconductors and nonsuperconductors are different. In fact, the 13 highest melting points in our sample are all superconductors. From the cumulative distributions one obtains $D=0.52$, yielding $\alpha_D=0.0058$. Similarly the large value of $\chi^2=12.70$, corresponding to $\alpha_{\chi^2}=0.013$, suggests a relation between melting points and superconductivity. Since melting temperatures are known to be related to bulk moduli it is of course not surprising that a similar relationship between both quantities and superconductivity is found.

Despite the fact that materials with the highest T_M's are all superconductors, the results in Table III indicate a small negative correlation between magnitude of T_c and T_M, however, the values of α found suggest that it is not statistically significant. Results for correlations between cohesive energy and superconductivity (not shown) are found to be very similar as those for melting temperatures, due to the fact that there is a large correlation between the two quantities ($\rho=0.98$ in the sample considered).

J. Atomic volume

There were some early speculations that a relation between superconductivity and atomic volume exists.[21] As seen in Fig. 11, elements with large atomic volume tend to be nonsuperconductors and those with small atomic volume are superconductors. This is not surprising considering the data for bulk moduli (Fig. 6), as materials with large atomic volume tend to have small bulk modulus and vice versa. The value of $\chi^2=9.27$ yields $\alpha_{\chi^2}=0.055$, and $D=0.41$ yields $\alpha=0.057$. Thus at close to the 5% level of significance a relation between atomic volume and superconductivity is found. The conditional probabilities suggest that systems with atomic volume larger than 40 Å^3 are much more likely to be nonsuperconducting.

However concerning the magnitude of T_c a *positive* correlation with atomic volume is found, as seen in Table III. That is, materials with larger atomic volume are likely to have a larger T_c. The results for both the r_S and τ coefficients indicate that this correlation is significant at the 5% level.

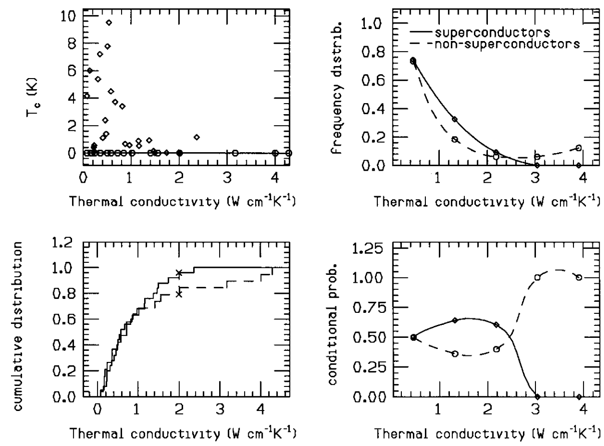

FIG. 12. Same as Fig. 2 for thermal conductivity in W cm^{-1} K^{-1}.

K. Thermal conductivity

The data on thermal conductivity (at room temperature) in Fig. 12 show similar behavior as those for electrical conductivity (Fig. 3), which is not surprising in view of the Wiedemann-Franz law. The low values of χ^2 and D, 4.78 and 0.17, suggest that there is no relation between existence of superconductivity in a material and its value of thermal conductivity. The conditional probabilities indicate a larger probability for systems of high thermal conductivity to be nonsuperconducting. However, the overall index of predictive association is rather low, $\lambda=0.16$.

Similarly as for electrical conductivity, a negative correlation is found between magnitude of T_c and thermal conductivity. The statistical tests indicate that this correlation is significant at the 2% level (Table III).

L. Magnetic susceptibility

The magnetic susceptibility of a metal has contributions from various sources, e.g., diamagnetism of ion cores, orbital diamagnetism and Pauli paramagnetism of conduction electrons. We have not attempted to separate the different contributions and instead used data for the total susceptibility at room temperature (from Ref. 32). Both the elements with highest (Pd,Sc) and lowest (Bi,Sb) susceptibilities are nonsuperconductors. The frequency distributions for superconductors and nonsuperconductors are very similar, as seen in Fig. 13, and the results for χ^2 and D indicate that there is no correlation between existence of superconductivity and magnetic susceptibility at even the 10% level.

While the Kendall τ and Spearman r_s coefficients are very small (Table III), the results for the correlation coefficient r indicate a positive correlation between magnitude of T_c and magnetic susceptibilty at the 5% level. This is consistent with BCS as well as other theories, as large values of the Pauli contribution to the magnetic susceptibility should arise from large electronic density of states which is also expected to favor large values of T_c.

M. Hall coefficient

Data for the Hall coefficient were obtained mostly from Refs. 33 and 34. We were unable to find data for Sr, Tc, Ba,

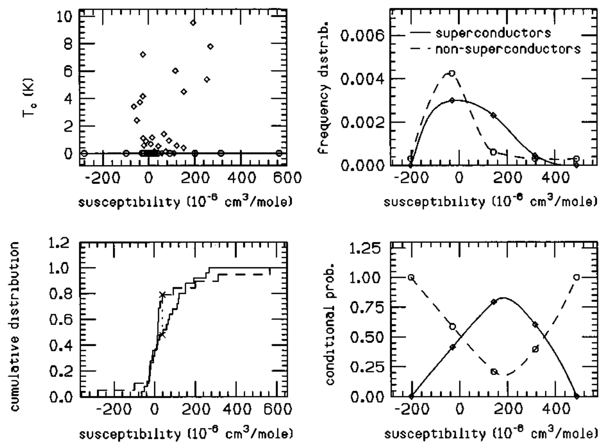

FIG. 13. Same as Fig. 2 for magnetic susceptibility in 10^{-6} cm^3/mol.

and Os, so that our sample set in this case has 40 elements, 23 superconductors and 17 nonsuperconductors. Unfortunately some of the Hall data in the literature exhibit considerable variation arising from experimental conditions or sample characteristics. We have taken the most recent data when conflicting results exist in the literature, if they appear reliable. When the data exhibit variation with temperature we have taken the value of R_H at the lowest (nonsuperconducting) temperatures, as they would presumably be more relevant to superconductivity. When variations with magnetic field exist we chose the high field value as it presumably would be less sensitive to the presence of impurities. For noncubic metals data for policrystalline samples were used.

There is no obvious relation between Hall coefficient and superconductivity within conventional BCS theory. However, such relations based on empirical observations have been suggested since early on.[38,39] Figure 14 shows a clear correlation between Hall coefficient R_H and superconductivity, in that materials with negative R_H tend to be nonsuperconductors and materials with positive R_H tend to be superconductors. This fact has been pointed out repeatedly by Chapnik.[39] The Kolmogoroff-Smirnoff D value of 0.78 is much larger than for any other property considered, and in-

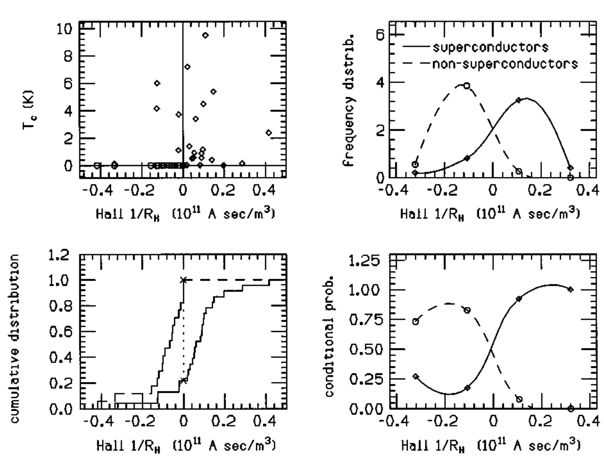

FIG. 14. Same as Fig. 2 for reciprocal of Hall coefficient $1/R_H$ in units 10^{11} Å s/m^3.

dicates that the null hypothesis of independence can be rejected at level of significance $\alpha = 1.3\times10^{-5}$.

The results for χ^2 depend strongly on the precise location of the bins used for grouping the data, unlike for any of the other properties. Specifically, if bins are placed so that the origin is at the center of a bin, the resulting χ^2 is much smaller than if the origin is at the boundary of a bin. The reason is that the origin is a dividing point between superconductors and nonsuperconductors. For this reason we have taken in this case four bins located symetrically around the origin (two on each side). The resulting $\chi^2 = 20.7$ is much larger than for all other properties, and yields $\alpha_{\chi^2} = 0.00013$. (Taking six bins yields $\chi^2 = 20.9$.) The index of predictive association is also rather large ($\lambda = 0.65$), indicating that knowing R_H gives significant information on the likelihood that the material is superconducting.

As another test we may consider just the sign of R_H, and test Chapnik's hypothesis that superconductivity is associated with $R_H > 0$ and nonsuperconductivity with $R_H < 0$. In our sample, 34 out of 40 elements are in agreement with this (the ones that are not are Ga, Sn, La, Hf, and Hg, superconductors with $R_H < 0$, and Sb, nonsuperconductor with $R_H > 0$). If the sign of R_H was unrelated to superconductivity, the probability of obtaining such or better agreement with this hypothesis is

$$P = \sum_{n=n_0}^{N} \frac{N!}{n!(N-n)!} \left(\frac{1}{2}\right)^N \tag{41}$$

with $N = 40$ and $n_0 = 34$, yielding $P = 4.2\times10^{-6}$.

If we denote by p the probability that a superconductor has $R_H > 0$ or a nonsuperconductor has $R_H < 0$, and $q = 1 - p$ its complement, the maximum likelihood estimators of these probabilities from our sample are

$$p = \frac{34}{40} = 0.85, \tag{42a}$$

$$q = \frac{6}{40} = 0.15. \tag{42b}$$

There is no explanation within BCS theory as to why p and q should be so different from 1/2.

On the other hand, the results in Table III indicate that there is no significant correlation between the magnitude of T_c and that of the Hall coefficient. The sample results are completely consistent with the hypothesis of independence.

IV. SUMMARY OF FINDINGS AND IMPLICATIONS

We have studied statistically the relation between normal state properties and superconductivity. Here we summarize various aspects of our findings.

A. Comparison of properties

The quantities listed in Table II give various quantitative measures of association between the existence of superconductivity in a material and normal-state properties. That is, they quantify in various ways how much the measurement of a given normal-state property can distinguish whether a material is or is not a superconductor.[40]

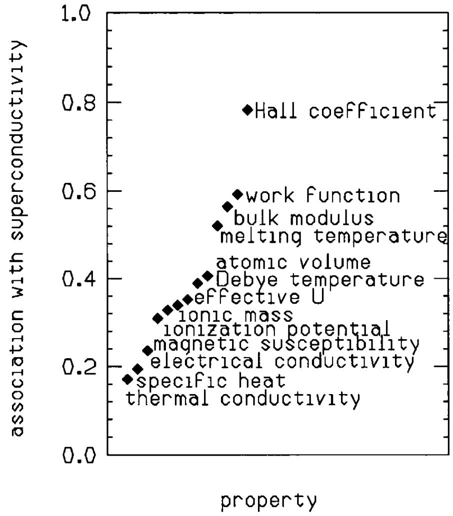

FIG. 15. Degree of association of normal-state properties with superconductivity as measured by the Kolmogoroff-Smirnoff index D. The horizontal axis scale is arbitrary.

How do these normal-state properties compare with each other concerning their association with superconductivity? The results obtained for the three indices calculated, φ (arising from the χ^2 test), the Kolmogoroff-Smirnoff D coefficient, and the index of predictive association λ, for the various normal-state properties, are roughly consistent with each other but show some differences in detail. The possible values of these indices range from 0 to 1, 0 reflecting complete independence and 1 complete dependence of the attributes. All three indices predict that Hall coefficient is by far the normal-state property most closely associated with the existence or nonexistence of superconductivity among all properties considered. The quantities most closely associated with BCS theory, electronic specific heat, Debye temperature, and electrical conductivity, rank consistently low in their degree of association with superconductivity according to these measures.

Because the Kolmogoroff-Smirnoff index is independent of any binning procedure it would appear to be the most reliable indicator of association. In Fig. 15 we plot the results for this index for the various normal-state properties. This can be interpreted as a ''ranking'' of normal-state properties concerning their association with superconductivity.

B. Significant findings

If we take the 5% level as statistically significant to reject the hypothesis of independence of superconductivity and a normal-state property, the results of our sample (Tables II and III) indicate:

(1) There is a relationship between the existence of superconductivity in a material and the following normal-state properties: bulk modulus, melting temperature, work function, and Hall coefficient. Namely, superconductivity is preferentially associated with larger bulk moduli, larger melting temperatures, larger (but not too large) work functions, and larger (positive) Hall coefficients. Also, since cohesive energies show a strong positive correlation with melting temperatures and bulk moduli, the same conclusions found for the latter apply to the former.

(2) Our sample results are consistent with existence of superconductivity being independent of the following normal-state properties: ionic mass, electronic specific heat, magnetic susceptibility, electrical and thermal conductivity, Debye temperature, ionization potential, second ionization potential, and atomic volume. (Atomic volume is almost at the borderline with our criterion, with small atomic volumes being favorable to existence of superconductivity.)

(3) The magnitude of T_c is positively correlated with electronic specific heat, magnetic susceptibility and atomic volume, and negatively correlated with electrical and thermal conductivity and Debye temperature.

(4) The magnitude of T_c is uncorrelated with ionic mass, ionization potential, second ionization potential, work function, bulk modulus, melting temperature and Hall coefficient.

Are these findings consistent with observations in other materials? Consider the following points:

(i) The fact that superconductivity is found in materials with very high electronic heat capacity (heavy fermion compounds) and low heat capacity (e.g., high-T_c oxides) is consistent with the conclusion that the existence of superconductivity does not depend on it. On the other hand, the low values of T_c in the heavy fermion materials, contrary to our conclusion (3) above, suggest that other factors not present in the elements may play a role.

(ii) The fact that there is a negative correlation between transport coefficients and T_c's is consistent with the fact that high-T_c oxides are poor conductors of electricity and heat, and more generally with observations in other classes of materials.

(iii) The negative correlation between T_c and Debye temperature is found in other classes of materials, e.g., $A15$ compounds.

(iv) The fact that superconductivity is associated with positive values of the Hall coefficient is found to be consistent with observations in high-T_c oxides (electron[41] as well as hole doped) and many other materials.[39]

(v) The fact that there is no correlation between ionic mass and magnitude of T_c, and that there is no positive correlation between Debye temperature and T_c, appears to be consistent with observations in other materials.

It is also interesting to note that for all properties where a significant correlation with existence of superconductivity was found, no corresponding strong correlation with the magnitude of T_c was detected; in fact, any correlation with magnitude of T_c tended to be of opposite sign. This suggests that most elements currently not known to be superconductors are likely to remain nonsuperconductors at temperatures lower than what has been attained so far.

C. Implications for theories of superconductivity

It would appear that the following findings are particularly relevant to the understanding of the fundamental mechanism(s) of superconductivity:

(1) The nonexistence of evidence for a negative correlation between ionic mass and magnitude of T_c nor of a positive correlation between Debye temperatures and magnitude of T_c are puzzling within the BCS electron-phonon framework. In other words, the fact that no statistically significant evidence is seen for higher values of T_c's being associated

with lighter ions in a material is surprising within the electron-phonon mechanism of superconductivity, since one would expect that other properties influencing T_c would average out over the sample. Also, attempts to find high T_c's in materials with light atoms such as metal hydrides have met with no success. Predictions of appreciable values of T_c for the light metal Li (Ref. 43) are contradicted by experiment. Predictions of high T_c in the lightest metal, metallic hydrogen,[44] are as yet unconfirmed and likely to remain so in light of the statistical evidence cited above. These observations need to be explained within the electron-phonon framework, if it is to be maintained.

(2) Similarly, the nonexistence of correlation between existence of superconductivity in a material and normal-state properties associated with phonons such as Debye temperature and electrical and thermal conductivities is puzzling within BCS-electron-phonon theory. One might have expected other properties expected to be detrimental to superconductivity, such as strength of Coulomb repulsion, to average out over the sample, leaving significant correlations with phonon-related properties to be detected.

(3) The fact that the distribution of bulk moduli, melting temperatures (and cohesive energies), and work functions are different in superconductors and nonsuperconductors does not seem to be explained by the existing theories of superconductivity and needs to be addressed.

(4) The existence of a strong correlation between sign of Hall coefficient and superconductivity is not explained by BCS electron-phonon theory. This is by far the most significant statistical correlation found. We discuss it in more detail in the next subsection.

D. Superconductivity and electron-hole symmetry

Within the conventional theory of superconductivity, the nature of the charge carriers in the sense whether they are electrons or holes, is irrelevant to the existence of superconductivity in a material. Thus the empirical very strong correlation between sign of Hall coefficient and superconductivity does not follow from it (nor from any of the other theories that assume implicitely electron-hole symmetry). One could imagine an indirect connection, for example that the electronlike or holelike nature of the carriers plays a role in determining the strenght of the electron-phonon interaction that enters the conventional theory. However, in the 40 years since BCS theory has been developed there has not been a single paper in the literature addressing the possible role of electron/holelike nature of carriers, or of the sign of the Hall coefficient, in the conventional theory of superconductivity. Given this fact we believe it is safe to conclude that the following statement is true, at least so far:

Within the conventional theory of superconductivity there is no correlation between existence of superconductivity in a material and the sign of its Hall coefficient.

If this is so, the empirical finding of such a correlation naturally casts doubt on this theory. Let us analyze this quantitatively using the method of Bayesian inference.[28] Divide theories of superconductivity into two classes, and define the following hypothesis:

θ_1: *conventional BCS-electron-phonon theory, or any other theory that does not differentiate between electrons and holes, and hence predicts that Hall coefficient and existence of superconductivity should be independent, describes superconductivity in nature.*

θ_2: *theories where the electron or holelike nature of the carriers play a role in superconductivity, and hence lead to Hall coefficient and superconductivity not being independent, describe superconductivity in nature.*

In the Bayesian approach to statistics, one assigns *a priori* probabilities for θ_1 and θ_2 $[P(\theta_1)=1-P(\theta_2)]$, and revises these probabilities in light of the obtained sample information. There is substantial prior information suggesting that θ_1 (in particular conventional BCS-electron-phonon theory) is correct, based for example on the detailed analysis of tunneling experiments.[42] Hence we may safely assume

$$P(\theta_1)>>P(\theta_2), \tag{43}$$

where $P(\theta_1)$ is dominated of course by the probability that conventional BCS-electron-phonon theory describes at least most superconductors. The estimation of *a priori* probabilities is a notorious difficulty in the Bayesian approach,[45] and we will leave them unspecified here except for the condition Eq. (43). Defining:

$Y=$ *result of our sampling experiment on the relation between existence of superconductivity and Hall coefficient,*

we have from Bayes's theorem

$$P(\theta_j/Y)=\frac{P(Y/\theta_j)P(\theta_j)}{\Sigma_i P(Y/\theta_i)P(\theta_i)}. \tag{44}$$

The probability that the sample results are obtained if superconductivity is independent of Hall coefficient can be estimated from Eq. (41) or from the value of α_D obtained for the Hall coefficient (Table III). Using the more conservative latter value

$$P(Y/\theta_1)=1.3\times10^{-5}, \tag{45a}$$

hence

$$P(Y/\theta_2)=1-1.3\times10^{-5} \tag{45b}$$

and from Eq. (44) we obtain

$$P(\theta_2/Y)=\frac{P(\theta_2)}{P(\theta_2)+1.3\times10^{-5}}, \tag{46a}$$

$$P(\theta_1/Y)=1-P(\theta_2/Y), \tag{46b}$$

where we have approximated $P(Y/\theta_2)$ by 1 with negligible error.

Eq. (46) implies that no matter how small the *a priori* probability for θ_2 was, the sample results lead to a very significant increase. If $P(\theta_2)$ initially was much smaller than 10^{-5}, Eq. (46a) implies that the *a posteriori* probability for θ_2 is increased by a factor 10^5. If the *a priori* probability for θ_2 to be correct is assumed to be of order 1 in 1 000 000, the *a posteriori* probability increases to 7%, while if $P(\theta_2)$ is assumed to be of order 1 in 100 000, the *a posteriori* probability is of order 50%. Thus, for any reasonable assumption about *a priori* probabilities, the results of the sampling leads to a considerable shift in the estimated probabilities for the two hypothesis: from being overwhelmingly likely, the conventional theory (together with other electron-hole symmetric theories) becomes less than certain, and a non-negligible probability is assigned to theories where electron-hole asymmetry plays a role, which were *a priori* of negligible likelihood. This result should hopefully lead scientists to in the future devote larger efforts to theories of superconductivity that make a distinction between electrons and holes, or to attempt to modify the conventional theory to explain the empirically observed electron-hole asymmetry.

V. A TEST CASE

We have argued in the previous sections that examination of the distribution of normal-state properties in superconductors and nonsuperconductors in a (small) sample set can yield useful information on whether a given normal-state property is connected with superconductivity. To gain further confidence in the soundness of this procedure we will now turn the problem around. Assuming a model of superconductivity where the effect of various normal-state properties is known, will the statistical correlations in our analysis show up as expected?

As a simple model let us assume that superconductivity is caused by a variable X that can be measured directly in a normal-state property. Let us furthermore asume that another property U is detrimental to superconductivity, and that superconductivity will only occur in a material if the condition

$$X-U>0 \tag{47}$$

is satisfied.Within the conventional picture the variable X could be the strength of the electron-phonon interaction, which can be estimated through measurement of the resistivity,[26] and the variable U could be a measure of the strength of the Coulomb repulsion. As the simplest situation, let us assume that X is uniformly distributed between 0 and 1, U is uniformly distributed between 0 and U_c, and X and U are uncorrelated. In order to match our best estimators for the probability of superconducting and normal materials, Eq. (4), we need to take U_c slightly smaller than 1, in fact

$$U_c=2[1-P(S)]=0.86. \tag{48}$$

Furthermore, we assume there is another random variable Y, uniformly distributed between 0 and 1, that affects the magnitude of T_c but not the existence of superconductivity. As a simple model we take for the critical temperature

$$T_c=10Y\sqrt{X-U}\ \ \mathrm{K} \tag{49}$$

so that when the condition for superconductivity Eq. (47) is satisfied, the magnitude of T_c is strongly affected by Y. The variable Y may be thought of as the density of states (measured through the specific heat) or the Debye temperature in the conventional picture.

The theoretical probability distributions for the variable X in the normal and superconducting populations are easily found to be

$$P_S(X)=\frac{X}{U_c(1-U_c/2)},\quad X\leqslant U_c,$$

$$\frac{1}{1-U_c/2},\quad U_c<X\leqslant 1\ \ ; \tag{50a}$$

$$P_N(X)=\frac{2}{U_c}\left(1-\frac{X}{U_c}\right),\quad X\leqslant U_c,$$

$$0,\quad U_c<X\leqslant 1. \tag{50b}$$

The conditional probabilities Eq. (3) are given by

$$P(S/X)=\frac{X/U_c[1-(U_c/2)]}{X/U_c[1-(U_c/2)]+[1-(X/U_c)]U_c/2},$$

$$X\leqslant U_c,$$

$$1,\quad U_c<X\leqslant 1\ \ ; \tag{51a}$$

$$P(N/X)=\frac{[1-(X/U_c)]U_c/2}{X/U_c[1-(U_c/2)]+[1-(X/U_c)]U_c/2},$$

$$X\leqslant U_c,$$

$$0,\quad U_c<X\leqslant 1 \tag{51b}$$

and the cumulative distributions by

$$P_S^c(X)=\frac{X^2}{2U_c(1-U_c/2)},\quad X\leqslant U_c,$$

$$\frac{X-U_c/2}{1-U_c/2},\quad U_c<X\leqslant 1\ \ ; \tag{52a}$$

$$P_N^c(X)=\frac{2X}{U_c}\left(1-\frac{X}{2U_c}\right),\quad X\leqslant U_c,$$

$$1,\quad U_c<X\leqslant 1. \tag{52b}$$

The probabilities that enter in defining the index of predictive association Eq. (28) are found to be

$$P(\mathrm{error}/X\ \ \mathrm{unknown})=\frac{U_c}{2}, \tag{53a}$$

$$P(\mathrm{error}/X\ \ \mathrm{known})=\frac{U_c}{4} \tag{53b}$$

so that the index of predictive association in this example is

$$\lambda_X=0.5 \tag{54}$$

independent of U_c. The Kolmogoroff-Smirnoff index D is obtained by maximizing the difference of the cumulative distributions Eq. (52), which occurs for

$$X_m=U_c(1-U_c/2) \tag{55}$$

and yields

$$D=1-U_c/2=0.568. \tag{56}$$

Figure 16 shows graphs of the various theoretical probability distributions for our model system for the variable X. For the variable Y instead, which is not related to occurrence of superconductivity, the theoretical probabilities in the N and S populations are of course identical (uniform), the index of predictive association is $\lambda_Y=0$, and the Kolmogoroff-Smirnoff index is $D=0$.

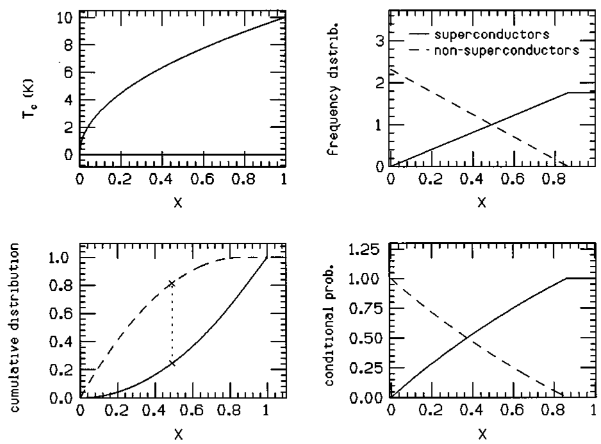

FIG. 16. Same as Fig. 2 for the theoretical probabilities for the test case property X of Sec. V. In the upper left graph we show only the maximum T_c for given X (solid curve) within this model: all values of T_c smaller than that value are allowed.

We now obtain random samples of 44 elements, 25 superconducting, and 19 nonsuperconducting, by generating random numbers X, U, and Y according to their probability distributions. For these samples we compute the same statistical quantities that we computed in our analysis of normal-state properties in the previous sections.

Figures 17 and 18 show results for a typical sample for the properties X and Y, respectively, and Tables II and III show the corresponding entries for these variables. It can be seen that property X clearly shows the signature of being associated with superconductivity in χ^2, D, and λ, while property Y shows no such association, as expected. On the other hand, property Y shows a strong correlation with the magnitude of T_c, evidenced in the Spearman rank, Kendall, and ordinary correlation coefficients. We have run several random samples such as this one and in each case the Kolmogoroff index D showed correlation between variable X and superconductivity well beyond the 5% level, while the variable Y showed no correlation with superconductivity at the 5% level, as expected.

Would it be possible to find no significant correlation between existence of superconductivity and the variable X in this model? In principle of course yes, in an extremely atypical sample. It would also be easily possible if the variables X and U are not assumed to be independent but positively correlated, so that large values of X would more often be associated with large values of U and nonsuperconductors would result. Indeed, any observation can be explained by invoking appropiate correlations.

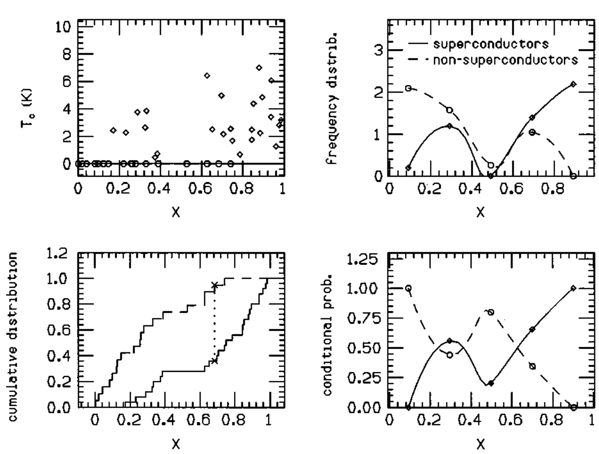

FIG. 17. Same as Fig. 2 for a random sample of 44 elements for the test case property X discussed in Sec. V.

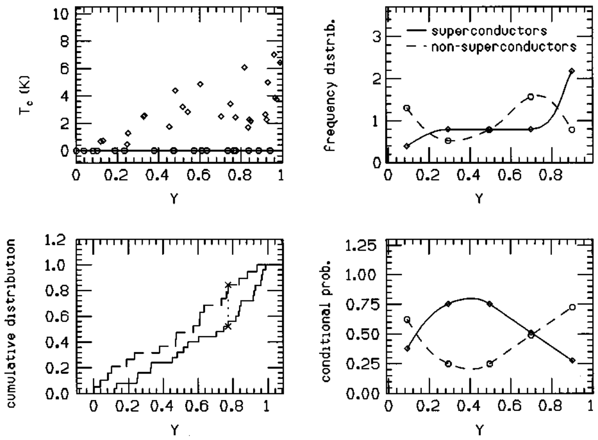

FIG. 18. Same as Fig. 17 for the test case property Y.

The degree of correlation of the variable X with existence of superconductivity in this test example is of the same order of magnitude as found for the normal-state properties work function, bulk modulus and melting temperature in the previous sections. On the other hand, Hall coefficient showed an even stronger correlation with existence of superconductivity. This suggests that the sign of the Hall coefficient strongly determines existence of superconductivity independent of the magnitude of other properties that could be influencing the magnitude of T_c. Concerning the magnitude of T_c in our test example, the variable Y showed similar correlations as were found for the specific heat in the previous sections.

VI. DISCUSSION

The understanding of superconductivity in solids is in a peculiar state. The conventional theory of superconductivity has been firmly in place for several years, and had been thought to describe superconductivity in all materials. In recent years, new families of materials have been discovered that do not seem to fit the conventional framework, and scientists have been working in developing new theoretical frameworks to describe the new materials. However, the applicability of the conventional theory to the ''conventional'' materials has not been called into question. Perhaps this is the time to do so.

The statistical analysis discussed in this paper casts some further doubt on the conventional theory as it stands to date. None of the observables naturally associated with BCS-electron-phonon theory was found to yield statistically significant information on whether a material is or is not a superconductor. The properties found to be most closely associated with existence of superconductivity, work function and Hall coefficient, are electronic properties, not obviously related to phonon properties. In particular, the strongest correlation found was with the sign of the Hall coefficient, for which the conventional theory in its present form has no explanation. It may be possible to explain these correlations within the conventional electron-phonon mechanism, but it has not been done so far. Unless these observations are convincingly explained in the conventional framework, they will increasingly stand out as anomalies of the type described in Ref. 46.

There are various directions in which the present work can be extended. First, other normal-state properties not discussed in this paper that may exhibit strong correlation with superconductivity should be considered. It would also be of great interest to apply this analysis to a larger class of materials than considered here. This is clearly feasible, but care must be taken not to bias the sample in any particular direction that might invalidate the findings. For example, an unbiased way to extend the sample would be to consider all superconducting materials known by 1975, listed in Robert's table.[47] Also, it would be of great interest to attempt to correlate superconductivity with more than one normal-state property at a time. For example, one could imagine that the magnitude of T_c could show no significant correlation with normal-state properties X and Y separately, and yet high T_c's would occur predominantly for large X and Y or small X and Y together. Hopefully, the present and future analysis along these lines will contribute to further our understanding of superconductivity to the point where theory will be able to predict (rather than ''postdict'') the superconducting properties of materials.

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); D. J. Scalapino, in *Superconductivity*, edited by R.D. Parks (Marcel Dekker, New York, 1969), p. 449, and references therein.

[2] P. W. Anderson, Physica C **185-189**, 11 (1991).

[3] D.J. Scalapino, Physica C **235-240**, 107 (1994).

[4] D. Pines, Physica C **235-240**, 113 (1994).

[5] S. Chakravarty and S. Kivelson, Europhys. Lett. **16**, 751 (1991).

[6] R. B. Laughlin, Physica C **234**, 280 (1994).

[7] N.F. Mott, J. Non-Cryst. Solids **164-166**, 1177 (1993).

[8] C.M. Varma, Phys. Rev. Lett. **75**, 898 (1995).

[9] T. Moriya, Solid State Phys. **26**, 51 (1991).

[10] A. W. Overhauser, Phys. Rev. B **42**, 10 130 (1990).

[11] R. Friedberg and T.D. Lee, Phys. Lett. A **138**, 423 (1989).

[12] J.C. Phillips, Phys. Rev. Lett. **72**, 3863 (1994).

[13] A.S. Alexandrov, J. Ranninger, and S. Robaszkiewicz, Phys. Rev. B **33**, 4526 (1986).

[14] D. Emin, Phys. Rev. Lett. **62**, 1544 (1989).

[15] E. Dagotto *et al.*, J. Supercond. **8**, 483 (1995).

[16] J. Labbe and J. Bok, Europhys. Lett. **3**, 1225 (1987).

[17] Y. Takada, J. Phys. Soc. Jpn. **61**, 238 (1992).

[18] H. A. Blackstead and J. D. Dow, J. Phys. Chem. Solids **56**, 1697 (1995).

[19] R. S. Markiewicz, Physics C **255**, 211 (1995), and referneces therein.

[20] J.E. Hirsch, Physica B **199&200**, 366 (1994), and references therein.

[21] B.W. Roberts, in *Intermetallic Compounds*, edited by J.M. Westbrook (Wiley, New York, 1967), p. 581, and references therein.

[22] T.H. Geballe, *Advances in Superconductivity*, edited by B. Deaver and J. Ruvalds (Plenum, New York, 1982), and references therein.

[23] B.T. Matthias, *Progress in Low Temperatures Physics* (Interscience, New York, 1957), Vol. II, p. 138.

[24] B.T. Matthias, in *Superconductivity in d- and f-band Metals*, edited by D.D. Douglass (Plenum, New York, 1976), p. 635.

[25] P.B. Allen and M.L. Cohen, Phys. Rev. **187**, 525 (1968); J.C. Carbotte and R.C. Dynes, *ibid.* **172**, 476 (1968); D. A. Papaconstantopoulos *et al.*, Phys. Rev. B **15**, 4221 (1977).

[26] B. A. Sanborn, P. B. Allen, and D. A. Papaconstantopoulos, Phys. Rev. B **40**, 6037 (1989).

[27] B. T. Matthias, in *Proceedings of the Georgetown University Summer Course on Science and Technology of Superconductivity*, edited by W.D. Gregory *et al.* (Plenum, New York, 1973), p. 263.

[28] W. L. Hays and R.L. Winkler, *Statistics, Probability, Inference, and Decision* (Holt, Rinehart and Winston, New York, 1971).

[29] L. Sachs, *Applied Statistics* (Springer, New York, 1982).

[30] B.W. Lindgren, *Statistical Theory* (Macmillan, New York, 1962).

[31] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986).

[32] *Handbook of Chemistry and Physics*, 59th ed., edited by R.C. Weast (CRC, West Palm Beach, 1978).

[33] C.M. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1973), and references therein.

[34] *Elektrische Eigenschaften I.*, edited by J. Bartels *et al.*, Landolt-Börnstein, Band 2, Part 6 (Springer, Berlin, 1959), and references therein.

[35] C.M. Varma, Phys. Rev. Lett. **61**, 2713 (1988).

[36] N. Koshida, Jpn. J. Appl. Phys. **27**, 690 (1988).

[37] B. T. Matthias, Helv. Phys. Acta **4** , 1030 (1968).

[38] I. Kikoin and B. Lazarev, Nature (London) **129**, 57 (1932).

[39] I.M. Chapnik, Sov. Phys. Dokl. **6**, 988 (1962); Phys. Lett. **72A**, 255 (1979); J. Phys. F **13**, 975 (1983); Phys. Status Solidi B **123**, K1L3 (1984).

[40] Note that since magnetic elements were excluded from our sample, the conclusions discussed here do not apply to materials that are magnetic.

[41] W. Jiang *et al.*, Phys. Rev. Lett. **73**, 1291 (1994).

[42] W.L. McMillan and J.M. Rowell, in *Superconductivity* (Ref. 1), p. 561.

[43] A. Y. Liu and M. L. Cohen, Phys. Rev. B **44**, 9678 (1991).

[44] N.W. Ashcroft, Phys. Rev. Lett. **21**, 1748 (1968); C. F. Richardson and N. W. Ashcroft, Phys. Rev. Lett. **78**, 118 (1997).

[45] J.O. Berger, *Statistical Decision Theory and Bayesian Analysis* (Springer, New York, 1985).

[46] A. Lightman and O. Gingerich, Science **255**, 690 (1991).

[47] B.W. Roberts, J. Phys. Chem. Ref. Data **5**, 581 (1976).