

PROPERTIES OF NONSUPERCONDUCTING TECHNICAL SOLIDS AT LOW TEMPERATURES

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Abstract

A number of physical and mechanical properties of materials used in low temperature applications are described with references to both theory and compiled data. These properties, which fall into three main groups, thermal, electrical, and mechanical, are given for pure metals, alloys, and a few nonmetals. In essence, this paper is a review of concepts and available data for low temperature engineering applications of nonsuperconductors.

I. Introduction

The field of applied superconductivity has seen tremendous progress in the past several years and much grander achievements seem waiting just over the horizon. Quite naturally, a great deal of effort has been devoted to understanding and improving superconducting materials for many diverse applications. The investigation of other components of low temperature systems, however, has not been as evident but, clearly, the designers and builders of such systems must constantly make decisions regarding the suitability of various nonsuperconducting materials for application at low temperatures.

In this paper some old as well as new information on a number of the more important properties of metals, alloys and a few nonmetals are presented. The properties fall into three main groups, thermal, electrical, and mechanical. Within each group, a number of properties, ranging from the commonplace to the relatively bizarre, are discussed. Where

The use of trade names in this paper of specific products is essential to a proper understanding of the work presented. Their use in no way implies any approval, endorsement, or recommendation by NBS.

it is practical, both a data compilation and a general introductory text are referenced for a given property. These references include many compilations of the NBS Cryogenics Division, wherein other publications are referenced. Frequently, a number of compilations exist in which a given property is treated. In Sections II, III, IV, and V only one or two of the most recent compilations are listed, but in Section VII a reasonably complete table of such compilations and their contents is given.

A good deal of existing information on these properties is not of much use to the designers of large magnets. For instance, many physics experiments have been done, over a restricted temperature range, on alloys of no technological importance, which resulted in information mostly of value to the understanding of metals. Therefore, such information is not included in this paper, and the discussion that follows relates only to materials which are used, or are likely to be used, in low temperature designs in the near future.

In Sections II, III, IV, and V, the various properties are described. In Section VI, some conclusions and suggestions for needed work are presented. In Section VII, a tabular description of the referenced data compilations is given.

An excellent descriptive text for all of the properties discussed herein is the book by Rosenberg.¹

II. Thermal Properties

In general cryogenic applications, some of the most severe engineering problems are related to thermal properties of materials. The time and amount of cryogenic fluid required to cool a structure and the possible catastrophic

effect of combining large temperature gradients and large thermal expansion coefficients are typical problems which must be considered. Of particular importance to magnet design, where current densities tend to be high, is the problem of removing heat from the interior of coil structures. This may be a transient problem, as with superconductors, or a steady state one, as with resistive cryogenic magnets.

Measurement of properties at 4K only is really not sufficient for modern problems. Liquid neon is already used with a large cryogenic aluminum magnet at NASA-Lewis, and it is quite likely that the future will see use of liquid hydrogen, slush hydrogen and supercritical helium (5-6K). Furthermore, in non-static operation, parts of a system may perform wide excursions in temperature and it is important to understand the possible effects of these excursions.

A. Thermal Expansion

The most recent general reference in the field of thermal expansion is a new text by B. Yates.² Other publications of interest are a compilation by Corruccini and Gniewek,³ which is the most complete work available on both metals and nonmetals up to 1961, and several later papers which present additional data on engineering alloys,^{4,5,6} epoxies,⁷ and other nonmetallics.⁸

The measurement of thermal expansion to the precision required for engineering applications is relatively easy. This precision is effectively the limit of material variability and is $\sim 0.1\%$. It is possible to make measurements with a precision near 1 part in 10^8 for the length change.

Thermal expansion data are invariably presented in one of two forms: the total expansion referred to room temperature

$$\frac{\Delta L}{L} = \frac{L(T) - L(293K)}{L(293K)}, \quad (1)$$

or the expansion coefficient

$$\alpha = \frac{1}{L} \frac{dL}{dT}. \quad (2)$$

A straightforward thermodynamic derivation of α leads to the result¹

$$\alpha = \frac{\gamma C_v}{3V\beta}, \quad (3)$$

where γ is the Grüneisen constant, C_v the specific heat at constant volume, V , and β the bulk modulus. As we will see in Section IV, this relationship can be used to estimate the specific

heat of materials for which α is known.

Figure 1 shows some broad generalizations about the behavior of various materials and Fig. 2 shows measured curves for a number of important materials. The curves of Fig. 2 are all from Corruccini and Gniewek³ except the one for 304L stainless steel, from Arp et al.⁵ and the TFE curve, which is from an extensive new compilation⁸ of the properties of six polymers of technological importance.

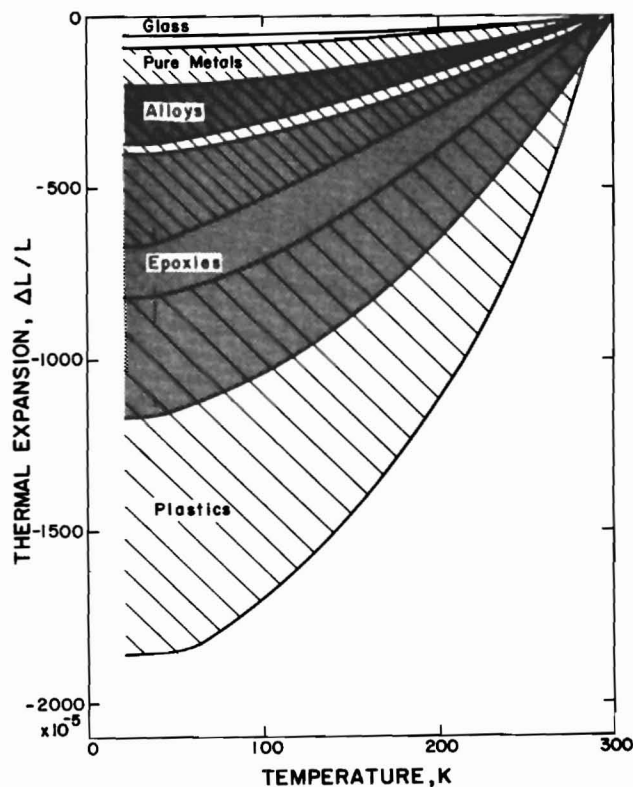


Fig. 1. General behavior of the thermal contraction for several classes of materials.

For most materials, the curve is quite regular and predictable. If, however, a transformation takes place on cooling, such as the martensitic transformation, then the curve will be complex. Some specialized materials such as the filled epoxies and alloys of the iron-nickel system can be produced with a wide range of possible values of $\Delta L/L$. Thus, these materials are useful for matching thermal expansion values of dissimilar materials, e.g., Kovar seals. Some nonmetals, such as Bakelite, match metallic expansion values very well and this is one reason they are frequently used. Magnetic fields are observed to have a negligible effect on

the expansion properties of most materials of the types considered here. The iron-nickel alloys, however, do show a significant magnetostriction effect.

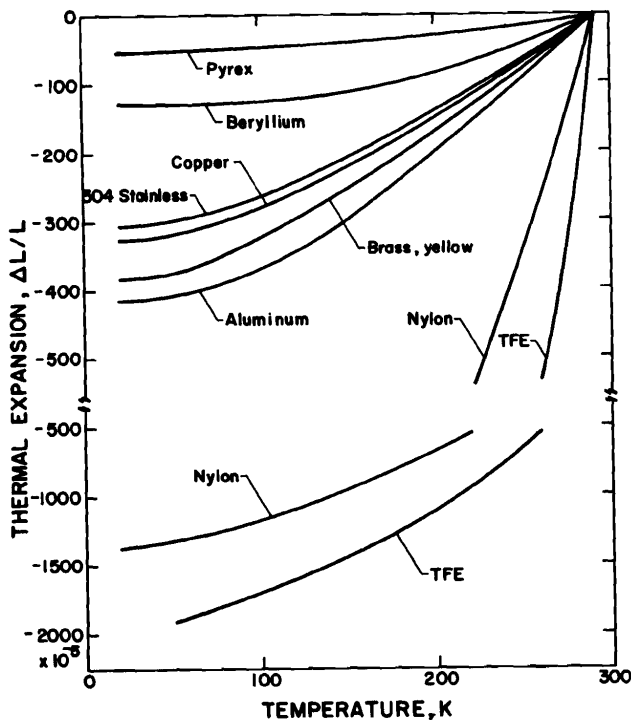


Fig. 2. Thermal contraction curves for specific materials.

There are a number of important generalizations which can be made concerning thermal expansion. Most of these have been demonstrated by Clark⁴ and are reproduced here. Large changes in composition are required to significantly affect the thermal expansion. Thermal treatment or the condition of an alloy has little effect unless it produces a structural change. The expansion coefficient at room temperature is a good indicator of the total length change to low temperatures. This result is very important to those with limited low temperature measurement facilities. It holds for nonmetals as well as for metals and alloys and the predicted length change generally is good to $\pm 5\%$. One further generalization of some importance is that, for design applications, one can consider all contraction as essentially finished by the time the material reaches 20K and, in fact, most of the contraction is effected by around 77 K.

Although most of the necessary information on thermal expansion at low temperatures

is available, there is some need for an up-to-date compilation on nonmetals in general and for some experimental work on the newer composite materials. The possible complexities of this latter group, particularly their anisotropic behavior, should not be taken lightly.

B. Thermal Conductivity

The two volume text edited by R. P. Tye⁹ is a good general reference that gives both theoretical and experimental information on thermal conductivity of solids and gases. The most recent and complete compilation on the low temperature thermal conductivity of technically useful materials is the new NBS monograph by Childs et al.,¹⁰ which is now in press.

Unlike thermal expansion, thermal conductivity is very sensitive to the state of the material, i. e., the number and type of impurities and defects and the degree of alloying and heat treatment. Because of this, one should be extremely suspicious of "average" curves for a given material. Experiments to determine thermal conductivity are quite difficult to perform with accuracy. Thus, typical low temperature thermal conductivity measurements are usually accurate to within $\pm 5 - 10\%$. Relatively high precision (1-2%) can be achieved but the apparatus becomes elaborate and the measurements very time consuming. As we will see later, it is often possible to predict the thermal conductivity fairly well from the electrical resistivity.

The theory of thermal conductivity is complex in that many separate mechanisms are operating simultaneously to transmit energy through the material. The basic quantity of interest is the thermal conductivity, λ , as defined by the heat transfer equation, which, in its simplest one dimensional form, is

$$\dot{Q} = \lambda(T) A \frac{dT}{dx}, \quad (4)$$

where, conventionally, \dot{Q} is the heat current in watts, A is the cross-sectional area in cm^2 , T is in Kelvin and thus λ has the units of watt/cm K . In general the thermal energy in a material is transported both by the lattice vibrations (phonons) and by the conduction electrons. These two modes operate as thermal resistors in parallel, such that the total thermal conductivity is

$$\lambda = \lambda_e + \lambda_g, \quad (5)$$

where the subscript g is the conventional designation for the lattice component (gitter is German for lattice). Each of these two contributions are

in turn made up of a number of separate components, reflecting the modes by which energy may be lost in transit. These are series additive such that the thermal resistivity, W , of, say, the electronic branch may be written,

$$W_e = \frac{1}{\lambda_e} = W(\text{electron-lattice}) + W(\text{electron-impurity}) + W(\text{electron-defect}). \quad (6)$$

The lattice contribution, λ_g , is small in pure metals, but may be significant in alloys, and in nonconductors (where $\lambda_e = 0$) it represents the total contribution. Typical curves for dielectric materials are shown in Fig. 3a. Figure 3b shows typical behavior of metals and alloys in which the electronic component is predominant. For nondilute alloys the lattice contribution becomes significant and the hump in the curve disappears. The curves of Fig. 3 are plotted vs T/θ where θ is the Debye temperature for the substance in question. While Debye temperatures are well known for elements,¹¹ practically no data exist for other materials of interest here. Note that the maximum value of λ is about the same for the two sets of curves. The impure dielectrics tend to have lower λ values than the impure metals by several orders of magnitude.

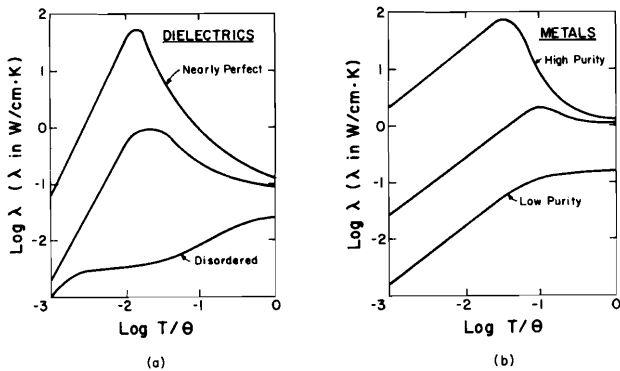


Fig. 3. General behavior of the low temperature thermal conductivity of two classes of solids. a. Dielectrics, in which the lattice component gives the total contribution, and b. Metals, in which the electronic component predominates in all but the most impure.

In Fig. 4 are curves, primarily from the monograph of Childs et al.¹⁰ for a number of materials. They are chosen to be representative, as far as possible, of a class of materials. The low temperature conductivities of pure metals, in particular, may easily vary over two or more orders of magnitude depending on purity.

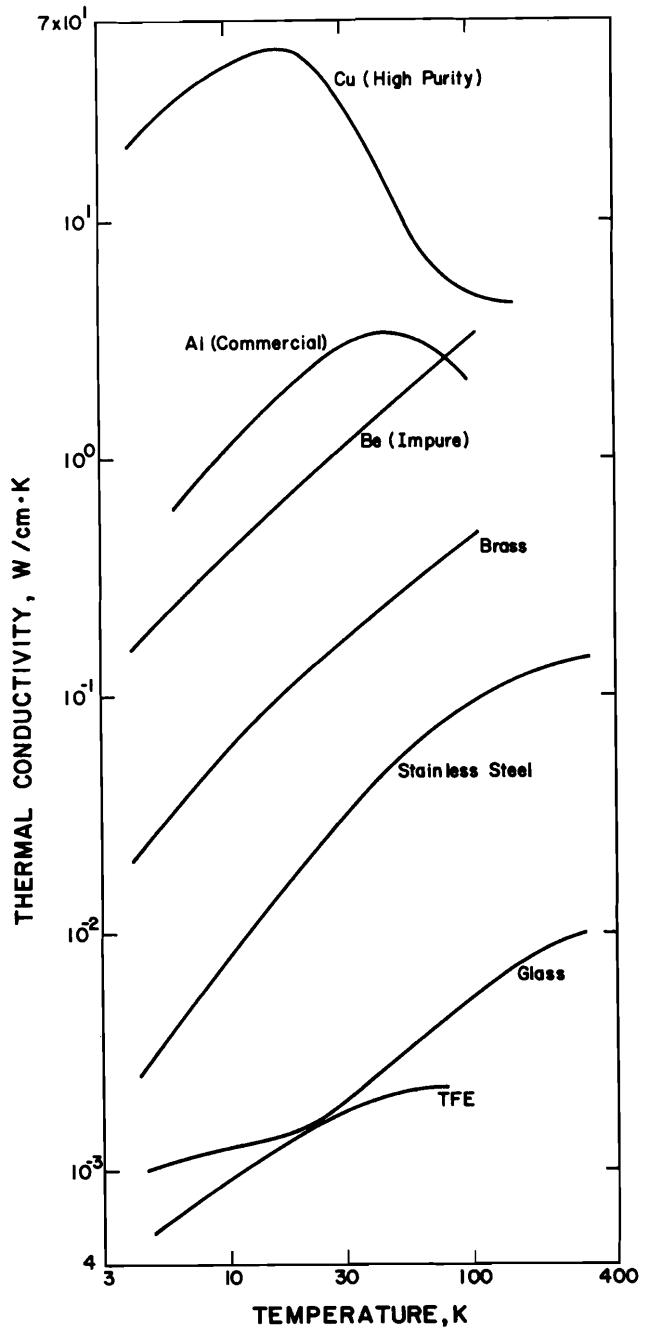


Fig. 4. Thermal conductivity values below room temperature for several classes of materials. For pure metals in particular the curves are drastically affected by purity.

For most pure conductors, the effect of a magnetic field on the thermal conductivity is very similar to its effect on the electrical conductivity, such that one can be predicted from

the other. This phenomenon of magnetoresistance is discussed in more detail in Section III and the Lorenz ratio predictive scheme is given in Section IV. It is important to note here that the effect may be very large for some pure metals with the thermal resistance at 4K increasing by a factor probably in excess of 100 for very pure copper at $H = 100 \text{ kOe}^{12}$ and by 6×10^4 for a gallium single crystal at $T = 1 \text{ K}$, $H = 13.7 \text{ kOe}^{13}$. In a similar vein, very pure metals show a low temperature size effect in thermal conductivity, i. e., the thermal resistivity increases as the specimen dimensions approach the mean free path. The work on this topic is reviewed by Brandli and Olsen.¹⁴ Note that size effects are no longer laboratory curiosities; common metals (Cu, Al) are available with purity values such that the mean free path of the electrons is in the range 0.1 - 1.0 mm, quite respectable dimensions even in an engineering sense.

A given engineering alloy may show a difference by a factor of two in λ at low temperature, depending on heat treatment and manufacturer.¹⁵ If the heat treatment is specified, a variation of 10-15% in λ should be expected from sample to sample. Often, the thermal conductivity can be predicted from the electrical resistivity and the Lorenz ratio for that class of materials.

There are surprisingly few measurements available on engineering alloys over the low temperature range. More are needed. It is also about time to start looking at the composite materials, particularly metal matrix, in some detail. Work also needs to be done on all conductors to determine whether or not the thermal magnetoresistance tracks the electrical magnetoresistance.

C. Specific Heat

The book by Gopal¹¹ is a fine general reference to the theoretical and experimental aspects of low temperature specific heat measurements. The NBS monograph on low temperature specific heat by Corruccini and Gniewek¹⁶ and the general compilation of low temperature properties edited by Johnson¹⁷ contain most of the existing data; the latter presents it in graphical form. The massive compilation of properties edited by Touloukian¹⁸ contains specific heat data, but does not emphasize the low temperature region. Unlike many other properties discussed in this paper, very few specific heat measurements have been reported on engineering alloys.

Most compilations give the specific heat

at constant pressure, C_p , and also tabulate values of the enthalpy, H , relative to some arbitrary temperature, usually chosen as absolute zero. The relationship is

$$H - H_0 = \int_0^T C_p dT, \quad (7)$$

where H is the enthalpy and T the absolute temperature. From an engineering point of view, enthalpy is the more useful concept since it represents the amount of thermal energy which must be removed from a structure in order to cool it from room temperature.

Measurement of specific heat by any of several comparative techniques is relatively easy. An absolute measurement is difficult. The compiled data are usually accurate to, at best, 1% below 20K and are somewhat better above that temperature. As we shall see in Section IV, it is possible to relate the specific heat and the thermal expansion such that one can be predicted from the other, usually with adequate precision for design purposes.

As was the case with thermal conductivity, the low temperature specific heat of a conductor has contributions both from the electrons and from the lattice. At most temperatures the lattice component is by far the larger. Theory gives,

$$C_v = \gamma T + aD(\theta/T) \quad (8)$$

where C_v is the specific heat at constant volume, $D(\theta/T)$ is the Debye function for the lattice contribution and a and γ are constants.[†] The Debye function and the Debye theory for specific heat are discussed in detail in the general references. For our purposes it is sufficient to point out that the Debye function varies at T^3 at low temperature and becomes constant at high temperature, such that C_v has the Dulong and Petit value of $3R$ where R is the gas constant (8.314 J/mol K). Further,

$$C_p - C_v = B^2 \beta VT \quad (9)$$

where B is the volume expansion coefficient, β the bulk modulus and V the sample volume. This difference is small at low temperatures but becomes significant as the temperature rises. It is necessary to keep this difference in mind because theory always gives C_v and experiments measure C_p . Thus at low temperatures we have,

[†] Note that this γ is not the Grüneisen constant used in the discussion of thermal expansion.

$$C_p \approx \gamma T + aT^3. \quad (10)$$

This relationship is usually well obeyed.

The complete curve for the lattice specific heat is shown in Fig. 5. The linear electronic component usually does not become significant until quite low temperatures. For copper, the two terms become equal at about 4K which is $T/\theta \sim 0.01$. The bar graph of Fig. 6 shows relative values for some common materials; note the logarithmic scale. Also shown in Fig. 6 is the percentage of thermal energy remaining at each temperature, with the room temperature value defined as 100%. These numbers are calculated from the enthalpy tables.¹⁶

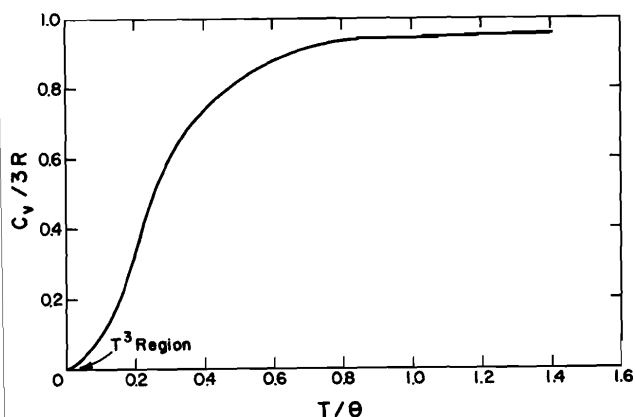


Fig. 5. Theoretical behavior of the lattice specific heat from the Debye theory.

As is the case with thermal expansion, the specific heat, to the precision of interest here, is not particularly sensitive to the state of the specimen. In general, the simple theories are well obeyed. Some materials do show anomalies,¹ but none in which we are interested here. Similarly, there is no reason to expect a magnetic field to affect the specific heat.

There are some interesting generalities and consequences connected with the specific heat behavior. One is that the specific heat of an alloy near room temperature can be reasonably well predicted by taking a linear combination of the specific heats of the constituents weighted according to relative abundance (Kapp-Joule rule). At low temperatures one can either proceed according to the above method or use a weighted average of the θ values. These methods all assume that no phase changes take place as a result of the alloying. Because the specific heat falls much more rapidly with decreasing

temperature than the thermal conductivity, thermal equilibrium occurs very quickly at low temperatures, i. e., the thermal diffusivity, discussed in Section IV, becomes very large. This also means, of course, that small heat inputs to insulated parts of a low temperature apparatus will result in large temperature rises.

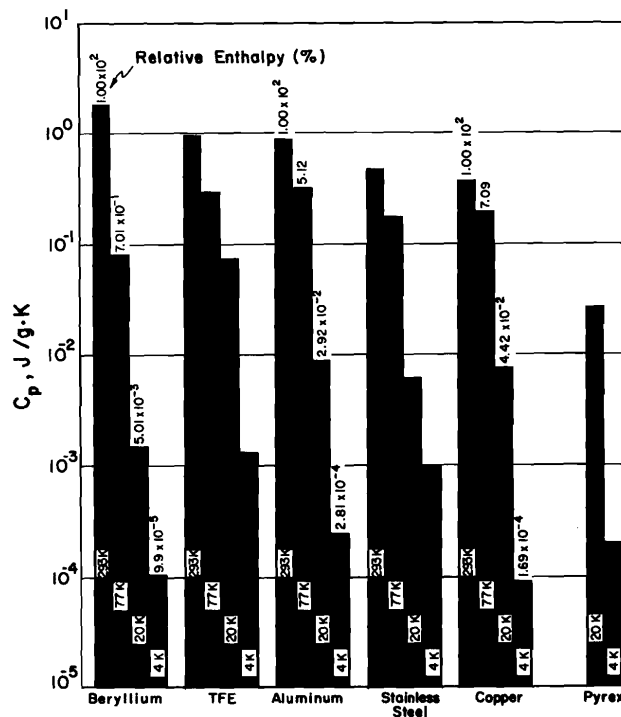


Fig. 6. Change of specific heat with temperature for a number of materials. Note that the vertical scale is logarithmic. The numbers give the enthalpy as a percentage with the room temperature value defined as 100%.

As mentioned earlier, measurements, at all temperatures, need to be made of the more recently developed materials such as composites. Alloy data are also needed for many of the engineering alloys, to which the additivity rules above do not apply due to phase changes or due to a multiplicity of components. Data are also needed on various other materials such as greases and bonding agents, some of which have been shown to behave anomalously at low temperatures.

D. Miscellaneous Thermal Properties

Here we will briefly outline a few other topics related to thermal properties of materials.

These are phenomena of concern to magnet builders and I hope the references will provide a sufficient path to further information.

Thermometry Many solids are used for thermometric applications at low temperatures: carbon, germanium and silicon, platinum, several dielectrics and various thermocouple combinations. The diversity of materials has come about because all have severe disadvantages. They may be too fragile or too expensive or not reproducible or have characteristics which are magnetic field dependent or require difficult or expensive instrumentation, etc. The actual application of solid state thermometers at low temperatures is a very tricky business because of the care required to insure that the thermometer is at the same temperature as the part being monitored. A good treatment of some of the problems is provided by Hust in his paper on the thermal tempering of electrical leads from thermometers.²⁰ The field of cryogenic thermometry in general is reviewed in a recent paper by Rubin²¹ which contains more than two hundred references to the literature.

Thermocouples are quite commonly used for low temperature thermometry when magnetic fields are not present. They offer the advantages of small size, low heat capacity, low cost and high accuracy. Two very recent NBS publications should be helpful to thermocouple users, the monograph on standard thermocouple types at low temperatures²² and a paper on the "gold-iron" materials developed specifically for the helium-hydrogen range.²³

The only solid state thermometers that are totally independent of magnetic field are the dielectric types. Thin carbon film resistors may also be field insensitive, but they are now only in the developmental stage. Carbon radio resistors, while not totally independent of field, are often used for a rough temperature measurement. Also, a great deal of information is available on their field behavior if corrections are desired.²⁴

Thermopower The thermopowers of some technical alloys have been measured. The measurement is usually made in conjunction with a thermal conductivity experiment since the added effort is not great. The data have no direct application in the engineering sense, although the thermopower occurs in the theoretical derivation of the Lorenz ratio. The reader interested in this work will find the general introductory text by MacDonald²⁵ a helpful starting place. A typical experiment on several aerospace alloys is

described by Hust, et al.²⁶

Kapitza Resistance The transfer of heat from a solid to highly conducting liquid helium II near the lambda point is observed to be impeded by a thermal resistance which is a property of the solid and/or its surface state. In fact, this resistance is usually the limiting factor in heat transfer under these conditions. The temperature region where this effect is important is quite limited (1-2K),[†] but many advanced apparatus designs use superfluid helium cooling. The effect is not well understood and is currently being studied by several groups. The interested reader will find the article by Snyder²⁷ and the references therein a more than adequate guide to the rather scanty literature.

III. Electrical Properties

Knowledge of low temperature electrical properties of materials is essential for a number of quite diverse reasons. First, pure normal metals, such as copper and aluminum, are invariably used to stabilize superconductors and, in some cases, as the (cryogenic) conductor itself for both dc and ac applications. Second, where time-varying fields are encountered, such as in pulsed magnets and machinery, eddy current effects may occur, not only in the conductors, but in the support structure as well, which may result in undesirable heating. In other instances, such as levitation schemes, slowly decaying eddy currents are desired. It is also necessary to know the effects of low temperatures on various properties of dielectrics, such as breakdown strength, if optimum designs are to be achieved. Electrical properties measurements, particularly dc resistivity, can also be used to monitor purity and degree of strain in pure metals, to determine the amount of precipitation hardening and amount of alloying in structural alloys and as a very easy means of predicting the thermal conductivity (see Section IV).

A. Metallic Resistivity, dc

The text by Meaden²⁸ has become almost a classic in this field. It contains excellent introductory material as well as a large amount of data. Three NBS publications, the two compilations by Hall^{29, 30} on pure metals and the

[†] Kapitza resistance again becomes important when He³ is added to the He II to attain very low (mK) temperatures as in dilution refrigerators.

paper by Clark et al.³¹ on engineering alloys, give most of the available low temperature data. Several other compilations are described in the table of Section VII, but engineering alloy data are surprisingly scarce.

The resistivity of pure metals in particular is affected by a bewildering variety of mechanisms, some of which will be briefly discussed here. To understand the full problem in all its complexity, see the review paper by the author on resistive mechanisms in aluminum.³² Because of these complications, compiled data are effectively useless in predicting the low temperature resistivity of pure metals; it must be measured each time. The usual quantity measured is the residual resistance ratio, or RRR, defined as

$$\text{RRR} = R(273\text{K}) / R(4\text{K}). \quad (11)$$

The philosophy behind this quantity is that $R(273\text{K})$ of a nominally pure metal is determined essentially entirely by the thermal vibrations of the lattice while $R(4\text{K})$ is determined entirely by the impurities and defects. Thus, the higher the ratio, the more pure the metal. As an example of the range of RRR which may occur, consider the case of copper. We have made polycrystalline copper wires with $\text{RRR} \sim 8000$ by a purification technique which uses a high temperature anneal in an oxygen atmosphere.^{1,2} By the same technique we have made single crystal copper specimens with $\text{RRR} = 60\,000$. Normal ETP copper has $\text{RRR} \sim 50$ and alloying may drop it to $\text{RRR} = 2$ or less.

Electrical resistivity experiments are among the easiest to perform of all measurements on solids. With most metals it is possible to attain a measurement uncertainty of 0.1% or better over the entire temperature range with a little care, and engineering measurements with 1% uncertainty are routine. However, the measurement of resistivity on very high purity metals near 4K is difficult, and, in fact, can only be done successfully by rather elaborate techniques.³³

The resistivity of most metals and alloys decreases as the temperature is lowered. Usually the approximation is made of a simple sum of a temperature dependent, or intrinsic, resistivity due to the lattice vibrations of the metal and a temperature independent part due to impurities and defects, so that

$$\rho(T) = \rho_i(T) + \rho_o. \quad (12)$$

This relationship is called Matthiessen's rule. It

is obeyed reasonably well by most metals, although occasional, usually small, deviations are seen.

The intrinsic resistivity is usually assumed to be given by the Bloch-Grüneisen theory which predicts

$$\begin{aligned} \rho_i &\propto T^5, & T << \theta \\ \rho_i &\propto T, & T > \theta \end{aligned} \quad (13)$$

with a more complex behavior between the two limits. This theory fits the data quite well for many common metals.

The temperature independent part of the resistivity, ρ_o , may contain contributions from many sources such as chemical impurities, point defects, dislocations, grain boundaries, etc., and much effort has been devoted to separating and studying these contributions. The most common, and best understood of these, are chemical impurities and the contribution in $\Omega\text{ cm/ppm}$ of each separate impurity adds to the total as

$$\rho_{\text{impurities}} = \sum_i (\rho/c)_i c_i \quad (14)$$

where c_i is the concentration in ppm of the impurity i . Tables of $(\rho/c)_i$ for various impurities in several metals are given by Blatt³⁴ and an updated table for aluminum is given by the author.³² The preceding discussion applies in detail only to dilute alloys. If the alloys are nondilute, then the behavior as a function of concentration of the alloying element depends strongly on the phase diagram of the alloy. Generally, ordered alloys give lower resistivities than disordered. Meaden²⁸ gives an excellent discussion of the situation.

Figure 7 shows the wide variation of resistivity which may be found for a given metal, in this case copper, depending on the state of the metal. All data are from A. F. Clark except that for the Kondo alloy.³⁵ Figure 8 shows typical resistivity curves for a number of commonly used metals and alloys.

Magnetic fields have a severe effect on the resistivity of pure metals and a much smaller effect on alloys. In general, the field causes the resistivity to increase, the relative increase being greater the higher the purity. This increase may continue with increasing field to the highest fields measured and for all purities, as is the case with copper, or the resistivity may become nearly field independent

as is the case with high purity aluminum. Many texts show so-called Kohler diagrams in which the magnetoresistance of many metals is plotted versus some quantity proportional to H/ρ (T).

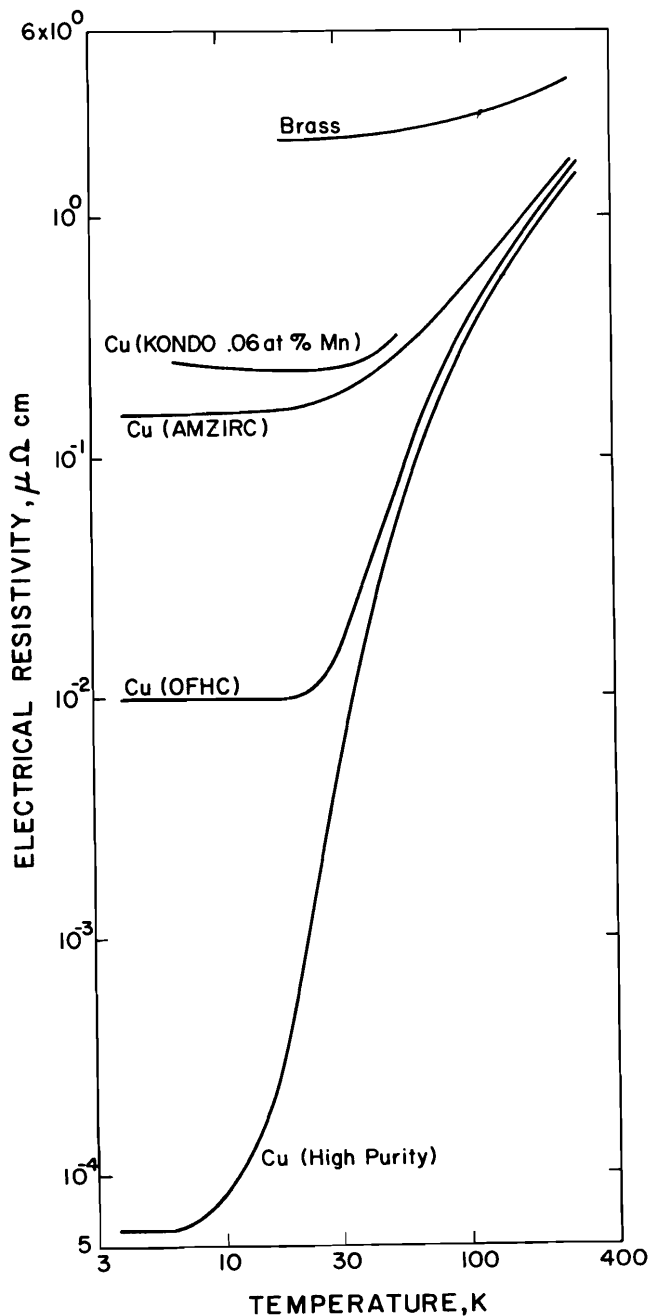


Fig. 7. Low temperature behavior of the electrical resistivity of a number of "pure" coppers and copper alloys.

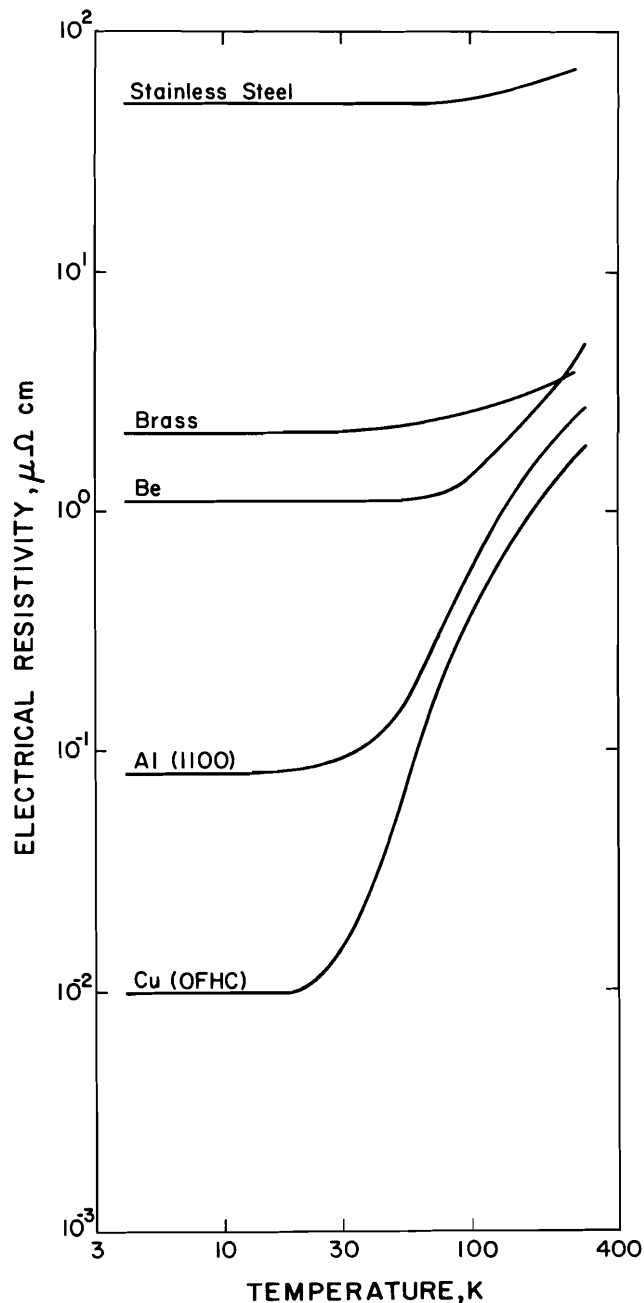


Fig. 8. Resistivity of several common metals at low temperatures.

In general, these plots are somewhat dated, and it is best to go to the literature for design data for a particular metal. Another paper by the author, to be presented at this conference, discusses the magnetoresistance of copper and aluminum in detail.³⁶ An important point, discussed in that paper, is that it is the resistivity at field which is important in choosing a metal and not the magnetoresistance, $\Delta R/R$. As

an example, high purity (RRR = 8000) copper has a $\Delta R/R$ of near 120 at 100 kOe but its actual resistivity at 100 kOe is significantly lower than that of oxygen free copper (RRR = 200) with $\Delta R/R \approx 5$.

In the pure metals, size effects,¹⁴ due to electron mean free paths on the order of conductor dimensions, become important. These effects give an added resistivity which is (probably) independent of temperature and which may represent better than half of the total measured resistivity in wires as large as 1 mm in diameter. The contribution, of course, becomes much larger in thin strips and filaments. Application of a magnetic field removes a good part of this additional resistivity - an effect which has not yet been studied in any detail and which is one of our current projects.

Stresses induced in high purity copper and aluminum by coil winding or by the magnetic field are observed to anneal out after some time at room temperature. Few experiments exist on this effect.

As we have tried to point out above, the pure metals do not give much opportunity for generalized statements regarding their electrical properties. On the other hand, the technical alloys investigated by Clark et al.³¹ do show a regularity of shape of the ρ versus T curves such that, given the room temperature resistivity of an alloy, it is possible to predict the entire curve to within about 5%. Of course, if phase changes such as martensitic transformations occur, the curve becomes complex and must be measured.

We still need information on several aspects of pure metals and alloys. A small amount of work has already been done, and more is needed, on pure metals reinforced with fibers or other inclusions such that the high purity of the matrix is not affected. An example of a resistivity measurement on these materials is the report by McDanel's³⁷ on copper reinforced with tungsten fibers. Some measurements should be made of the magnetoresistance of pure conductors under stress and on the effect of the field on electrical properties of structural materials, such as stainless steel, used in magnet winding. Recent information indicates that the magnetoresistive behavior of pure metal strips should be looked at for possible field direction anisotropies.

B. Metallic Resistivity, ac

Here we are concerned with effects occurring in the low frequency region, say $f < 500$ Hz.

This is the region of interest for ac power transmission and pulsed magnet systems. Alloy materials usually have essentially dc characteristics under these conditions. However, in cold support structures, one must consider the possibility of eddy current heating which can cause large temperature excursions and tend to promote dimensional instability. Eddy current problems are treated in detail in many texts on electricity. The book by Lammeraner and Staffl³⁸ gives calculations for a number of realistic situations.

Pure metals are commonly used as the stabilizing material in twisted-stranded superconducting cables for ac applications. The situation here is much more complex than the dc case in that one must make a trade-off between eddy current losses, dc resistivity and thermal conductivity. Each application seems to demand a new evaluation. My purpose here is to point out the characteristics of pure normal metals under common use conditions, which often require very thin conductors with long bulk mean free paths for the electrons. Three parameters are important: the electron mean free path, ℓ ; the sample dimension, d ; and the classical skin depth from electromagnetic theory,

$$\delta = (2\rho / \mu_0 \omega)^{\frac{1}{2}}. \quad (15)$$

Here ρ is the dc resistivity, μ_0 the permeability of free space (since we are dealing with nonmagnetic materials), and $\omega = 2\pi f$, where f is the frequency of the ac signal. At low frequencies $\delta > d$, we have an essentially uniform current distribution and dc theory applies. If $\ell > d$, the dc size effect must be considered. When $d > \delta > \ell$ we use the classical skin effect theory where the current is confined to a surface layer and thus the ac resistance increases with increasing frequency and the effective resistance of the surface layer is

$$Z = (\mu_0 \omega \rho / 2)^{\frac{1}{2}}. \quad (16)$$

When $d > \ell > \delta$ the situation becomes more complex, requiring use of the anomalous skin effect theory and its complex calculations.¹ The problem has not been solved in complete generality, but when $\ell \gg \delta$ the surface resistance, under a number of assumptions, becomes

$$Z = [\sqrt{3} \mu_0^2 \omega^2 (\rho \ell)_\infty / 16\pi]^{1/3}, \quad (17)$$

where $(\rho \ell)_\infty$ is a number which is assumed to be a constant for the metal and is the product of the bulk resistivity and the bulk mean free path i.e., in an infinite specimen. The

interesting feature of this result is that the surface resistance no longer depends on the purity of the metal. This expression gives a higher resistance than Eq. 16 because fewer electrons are contributing to the current. All this is not an exercise in frivolity; the condition $\lambda > \delta$ under which the anomalous skin effect theory should be used can occur at quite low frequencies. Arp³⁹ has calculated that for aluminum at 4K with RRR = 14 000, the theory is necessary if $f > 4$ Hz, with RRR = 45 000 it is necessary if $f > 0.1$ Hz.

To my knowledge, little work has been done on the effect of high magnetic fields on the ac properties of the high purity metals. It seems certain that the effects will be large and this is work which should be done soon.

C. Dielectric Properties

Information on low temperature electrical properties of dielectric materials are scattered here and there throughout the literature. The compilation by Schramm et al.⁸ on plastics and the references therein provide a good source of data. Here we present some rather generalized statements relating most directly to polymers but usually true for other dielectrics as well.

The low temperature electrical data of interest are on such quantities as dielectric constant, loss tangent, dielectric strength and volume resistivity. The dielectric constant tends to be reasonably temperature independent below about 200 K. The loss tangent goes through a number of oscillations with decreasing temperature down to 200-300 K and appears to decrease uniformly below that, although very little information exists below about 100 K. The dielectric strength may either remain constant or increase quite rapidly as the temperature is lowered from room temperature, depending on the material. The same general behavior is seen for the volume resistivity although the data are very limited.

IV. Relationships Between Physical Properties

There are a number of relationships between the properties discussed in the last two sections, which are frequently helpful to the user. Generally, they define a useful combination of properties, such as the thermal diffusivity, or a predictive scheme in which a difficult to measure quantity is determined from the measurement of an easy one, such as with the Lorenz ratio. Usually the results of the predictive schemes are sufficiently accurate for engineering applications.

A. Thermal Diffusivity

Thermal diffusivity is frequently presented as a separate property in low temperature compilations, although it is, in fact, a combination[†] defined by

$$\alpha = \lambda/d C_p \quad (18)$$

where d is the density. The diffusivity, α , is in essence a measure of how rapidly the substance approaches thermal equilibrium after a perturbation. Thus, α is an important quantity when one is concerned with transient behavior. Note that, as the temperature decreases, α usually becomes very large because λ is not as greatly affected by temperature as C_p which tends to decrease by many orders of magnitude.

The table of Section VII indicates those compilations in which the thermal diffusivity is presented separately.

B. Thermal Expansion - Specific Heat

By considering the thermodynamic properties of solids one can arrive at two rules, relating the volume expansion and the enthalpy, H , the Grüneisen⁴⁰ rules. That these two quantities should be related is not surprising; they both are determined by the thermal state of the lattice. The experimental validity of the relationship has been proven quite well for pure metals. Clark and Kropschot⁴¹ use the equation

$$\frac{V_T - V_0}{V_T} = \frac{H}{Q_0 - kH} \quad (19)$$

in which Q_0 and k are, theoretically, constants, to determine the temperature dependence of Q_0 for a number of metals and alloys. Q_0 turns out to be nearly constant with temperature and k is quite small at low temperatures, so that the kH term is negligible. They further use room temperature data on specific heat and thermal expansion data to make quite acceptable predictions of the low temperature specific heat of a wide range of alloys. They do not discuss the errors to be expected in general, but the technique seems to be one which could be very useful for engineering applications.

[†] In high temperature research, the thermal diffusivity is the measured quantity and the thermal conductivity is the one calculated.

C. Lorenz Ratio

It is reasonable to assume that the electronic contribution to the thermal conductivity and the electrical conductivity should be related, since the conduction electrons are the carriers in both cases. The equation expressing this relationship is the Wiedemann-Franz-Lorenz law

$$\frac{\lambda \rho}{T} = L \quad (20)$$

where, by simple theory, the Lorenz ratio, L , should be a constant. Sommerfeld calculated the free electron theory value to be $L_0 = 2.443 \times 10^{-8} \text{ V}^2/\text{K}^2$. Needless to say, L is not altogether constant, but it is the most constant of the trio, λ , ρ , L . For some simple metals L is also apparently independent of magnetic field, although this is one of the areas which still needs much more investigation. In any event, if one knows the L vs T curve for a given alloy group, and the electrical resistivity vs T for a particular alloy, it is quite possible to predict the thermal conductivity with sufficient accuracy for many applications. Typical curves of L vs T for various substances are shown in Fig. 9. The behavior of pure metals is indicated by the curves for Al and Cu; as purity increases, the minimum drops and moves to lower temperatures. Predictive schemes using the Lorenz ratio are discussed by Powell¹⁹ and by Hust and Clark.⁴² A compilation of Lorenz ratio data as a function of temperature for a wide variety of metallic materials has been completed recently by Hust and Sparks.⁴³

V. Mechanical Properties

With this topic we enter a somewhat different realm than that of the previous sections. The measurement of mechanical properties has had quite a different history than that of physical properties. The emphasis has tended to be on tests to compare existing materials and not so much on the determination of rules and equations by which general classes of behavior can be described. This is not to imply that theoretical work does not exist in this area, but the problems are extremely complex and the simplifications necessary to make them tractable usually preclude applications to engineering materials. In many instances the important variables in a process, such as crack initiation, are not well understood, and thus much of the available experimental information tends to be restricted to very specific materials and circumstances. A bewildering array of "standard" tests exist for about 25 mechanical properties of solids, and

data compilations abound, as do uncompiled publications.

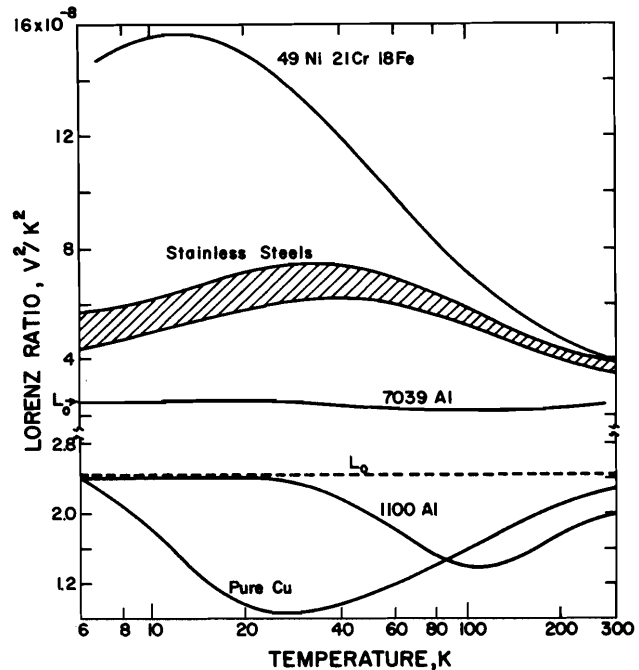


Fig. 9. Typical Lorenz ratio values for various materials. Note the scale is offset and changed at one point on the vertical axis.

What I intend to present here is a discussion, at a very elementary level, of the more important of the common mechanical properties for low temperature work. Curves showing typical behavior will be presented.

Two review papers on mechanical properties were presented at an earlier Brookhaven conference, one on metals⁴⁴ and one on nonmetals.⁴⁵ An ASTM publication referenced earlier¹⁹ also contains several articles of a general nature. Detailed texts on low temperature mechanical properties also exist.^{46, 47} The two compilations containing the most low temperature data on engineering alloys are the Cryogenic Materials Data Handbook⁴⁸ and the Materials Properties Data Handbook.⁴⁹ Other sources of data are shown in the table of Section VII. In many instances, extensive compilations exist on low temperature properties of particular materials, such as the work on copper and alloys by Reed and Mikesell⁵⁰ and the recent article on aluminum by Reed.⁵¹

A. Tensile Properties

Here we include all of the properties generally associated with a classical tensile test. A very generalized stress-strain diagram is given in Fig. 10. This particular shape, typical of alloys and some plastics, will serve to define the terms used in the data compilations. As force is applied to the material, a region of elastic behavior first occurs as shown by the line AB of Fig. 10. The slope of this line defines the Young's modulus, or modulus of elasticity, for the material.[†] As the stress is increased, the material enters a plastic region, at a point called the proportional or elastic limit (B). The stress then reaches a maximum and declines until the specimen fractures. The maximum stress (point D in the figure - some plastics may have multiple maxima, in which case the greatest stress is used) is the tensile strength. The yield strength is the stress at which the specimen has undergone some small plastic deformation, typically 0.2% (called the "offset"), as at point C (some authors use the first maximum, such as point D, as the yield stress and some don't define it at all). Breaking strength is the stress at fracture (point E). Similar diagrams made in compression or torsion serve to define similar quantities such as the compressive modulus and the shear modulus, respectively. Other quantities of interest can also be determined from the stress-strain curve. Ductility, the measure of the amount of plastic deformation which can occur before fracture, is given by the elongation (the distance BE), and toughness, a measure of the energy required to stress the specimen to fracture, is given by the area under the stress-strain curve.

Figure 11 shows typical stress-strain curves for various materials at 20 K. The curves are from the Cryogenic Materials Data Handbook.⁴⁸ The jog in the AISI 304 curve, representing a strain region over which no work hardening occurs, is probably associated with one of the martensitic transformations which occur in 300 series stainless steels. Cold-working of the metals gives significant increases in the maximum stress. Figure 12 shows the typical behavior of fcc and bcc metals as a function of temperature. Some generalizations are possible here. The stronger materials, particularly the nonmetals, tend to be most brittle. The fcc metals show an increase in

[†] All of the definitions use the engineering stress, i.e., the initial cross section area and initial length of the specimen are used in the computations of σ and ϵ .

flow stress and tensile strength with decreasing temperature, with some increase in ductility. The bcc metals, while also showing increased strength, show drastically decreasing ductility and a transition to brittle behavior as the temperature is lowered. The hcp metals, with the exception of titanium, tend to have generally low ductility even at room temperature. The ductile-brittle transition temperature is affected by many variables and it is usually these variables that determine the serviceability of an alloy for low temperature use. Several authors discuss materials selection problems in detail detail.^{44,47,52} Also of considerable importance in applications is the behavior of welds in the various alloys; the alloy itself may be quite acceptable for use at cryogenic temperatures but the welds are not.⁴⁴ Often data on weld tensile tests are presented in the compilations.

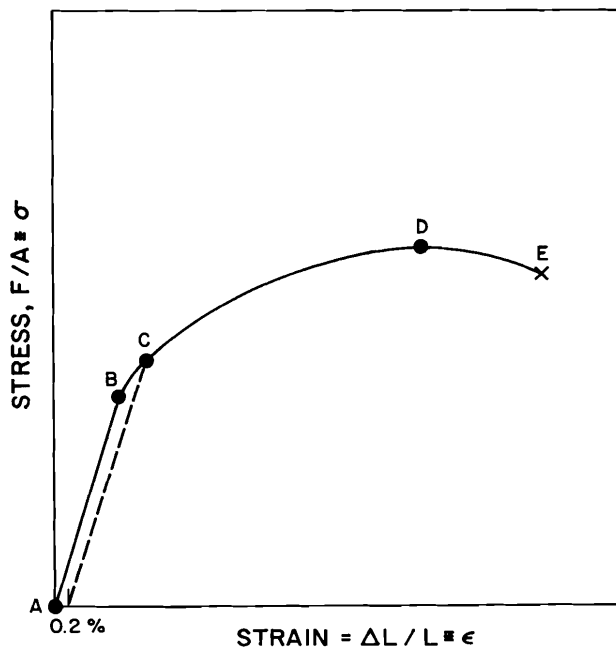


Fig. 10 Generalized stress-strain diagram.

Other types of tensile tests are also compiled in the literature. The most common are the notch tensile tests and the flexural strength tests. These tests and their significance are described in standard texts on mechanical properties.⁵³

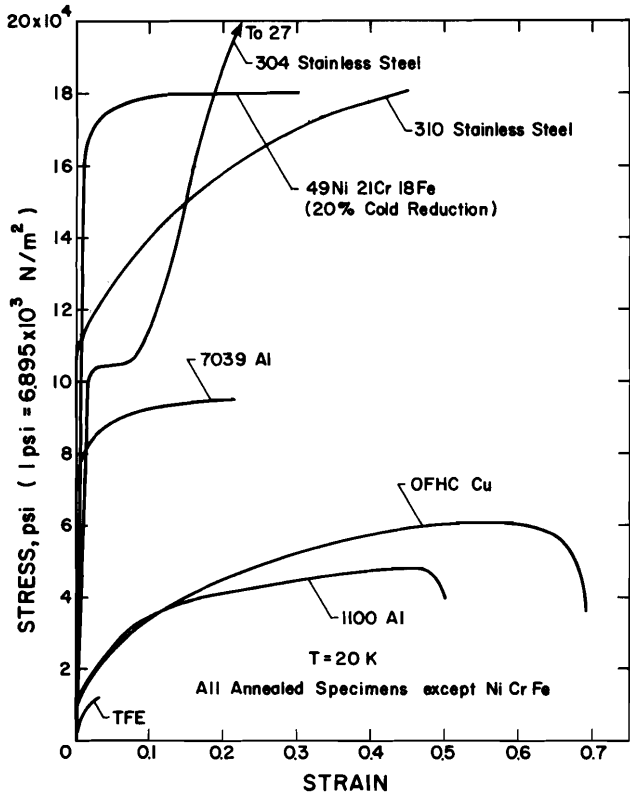


Fig. 11. Typical stress-strain curves for a number of materials at 20 K.

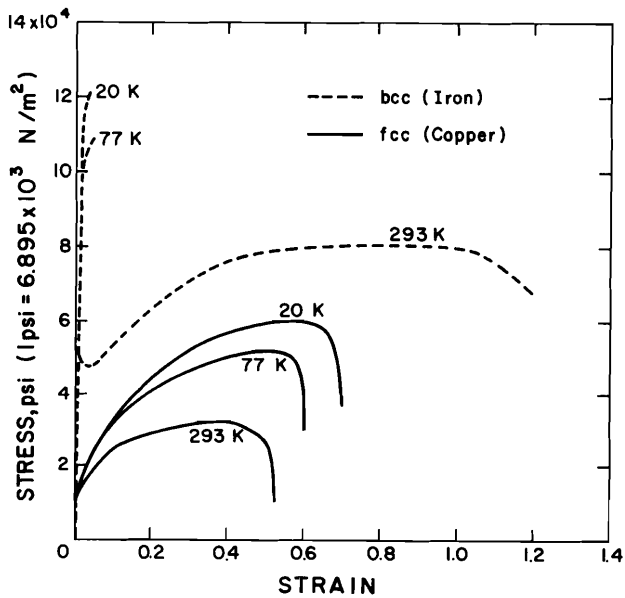


Fig. 12. Tensile behavior of bcc and fcc metals as a function of temperature.

B. Fatigue and Creep

Fatigue and creep describe the behavior of metals under loads below those which cause fracture in a tensile test. Fatigue is the gradual failure of a material under cyclic application of stress. Creep is the increase of strain with time under constant load. A similar, but less often discussed, property is stress relaxation which is the decrease of stress with time under constant strain. A majority of the in-service failures at low temperatures occur under fatigue or creep loading conditions.

Low temperature fatigue data are available for a large number of metallic materials, but usually only down to liquid nitrogen temperature (77 K). A typical fatigue strength plot for a few materials is shown in Fig. 13.

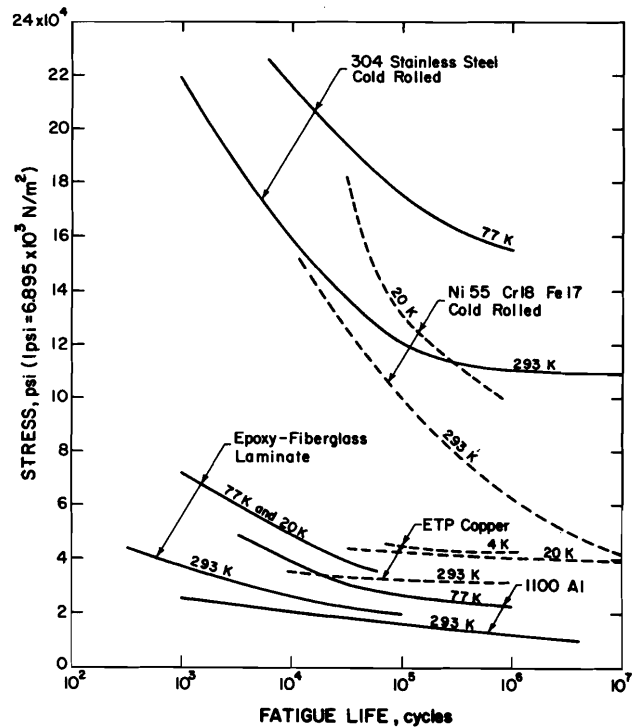


Fig. 13. Fatigue strength data for several materials

The data are from the Cryogenic Materials Data Handbook.^{4,8} Again, some general behavior characteristics can be stated. Metals which do not become brittle exhibit a greatly increased fatigue life as the temperature is lowered. Metals with a ductile-brittle transition behave exactly as ductile materials above the transition and show a very narrow range of fatigue strength below that, tending to fracture almost immediately, or not at all, depending on the stress level. Little low temperature information is available on nonmetals.

The fatigue mechanism involves the initiation and growth of microcracks in the materials. The growth process is quite well understood theoretically but the same is definitely not true of the initiation of the cracks

A general compilation of low temperature creep data on engineering materials is not available. Several stages of creep occur, and the process is highly temperature sensitive. The most likely low temperature process in metals is the logarithmic, or primary, creep which occurs below about $0.4 T_m$ where T_m is the melting point. Here the creep work hardens the metal and the creep rate decreases rapidly. Above $0.4 T_m$ the creep tends to become linear with time. In the cryogenic temperature region this situation is likely to occur only for metals used as seals, such as indium, or other low melting point metals used in special applications. Creep also occurs in polymers at low temperatures. The theoretical treatment is somewhat different.⁴⁷ As one would expect, creep is worse in the polymers such as TFE, which remain flexible at low temperatures.

Creep data typically are presented as curves of strain versus time, at a particular constant stress, at several temperatures.

C. Fracture Toughness

A number of testing procedures use notches as stress concentrators. Notch tensile strength and impact strength test data are available for many materials. The concept of fracture toughness has only fairly recently been developed into a test procedure. Here the idea is to duplicate, as far as possible, actual crack conditions in a material and then determine the critical crack length and stress which will cause the crack to propagate. Cracks of various sizes can exist within a material and still not require removal from service; it is only when the cracks start to grow that the problems become critical. The field of fracture toughness from theory to testing methods is reviewed in a relatively recent ASTM publication on the subject⁵⁴ and in the text by Wigley⁴⁷. The tests have considerable potential for helping in the design of new and more reliable nondestructive testing techniques, since fracture toughness tests closely approximate the actual in-service behavior of the material.

The basic test involves introducing a crack in a material and determining its growth as a function of stress and temperature. The two parameters usually presented are the critical stress intensity factor K_C , also called the fracture toughness, or the crack resistance force G_C ,

versus various parameters relating to specimen size or versus temperature. K_C is related to the fracture stress and

$$G_C = K_C^2 / E \quad (21)$$

where E is the Youngs modulus of the material, G_C is thus related to the rate of energy release.

It is only recently that fracture toughness tests have been standardized and much of the early data must be treated with some caution. One should read the introduction to the Cryogenic Materials Data Handbook⁴⁸ before using the data therein. The behavior of K_C with temperature is complex; it depends on specimen size and shape as well as the basics of the propagation. Thus, it is not possible to present any generalizations of behavior. Each material must be measured and evaluated separately.

VI. Summary

I have attempted here to provide an overall picture of the properties of nonsuperconducting materials. A significant amount of data exists on a surprising number of materials, but there are also large gaps in our knowledge which should be filled before long. The general class of composite materials requires a great deal of work. These materials have many properties which make them ideal for support structures at cryogenic temperatures, applications in large temperature gradients and for high strength conductors. Another field in need of more investigation is the measurement of the change of various physical and mechanical properties under intense irradiation at low temperatures. The study of crack propagation at low temperatures is a relatively new field in which reliable specimen-independent tests are needed. The electrical properties of structural and stabilizing materials associated with superconductors need to be carefully evaluated, particularly in the presence of time-varying magnetic fields.

In many instances, data exist in the literature, particularly in relatively obscure reports. There is a definite need for compilations and critical reviews of many properties, perhaps in the form of updating of existing compilations. This is, at best, a thankless task but one which is invaluable to the "consumer".

The Cryogenic Data Center of the Cryogenics Division of NBS at Boulder, Colorado 80302, will produce custom bibliographies on various subjects at nominal cost. The stored information is not complete in the field of mechanical properties but it is complete and current regarding physical properties and cryogenic devices.

VII. Tabulation of Data Sources

Table 1 presents a general survey of the available sources of low temperature data on the properties discussed here. Hopefully, it contains all of the major, readily accessible, compilations. Also included are a number of papers which are not true compilations but which contain information on a number of materials and which were referenced in the text.

The use of the table is obvious, the numbers refer to the reference list at the end of the paper. Also included are titles of the references to facilitate the reader's choice for a particular application.

Some effort has been made to avoid compilations which duplicate completely the presentation of another, either in content or form but this is difficult to accomplish. Thus, it is suggested that before one tries to take a weighted average of data for a given property, he should be certain to check the actual sources.

VIII. Acknowledgements

Thanks are due to most of the staff of the Cryogenic Properties of Solids Section, Cryogenics Division, NBS, for their helpful input to various parts of this paper. A. F. Clark, J. G. Hust, R. L. Powell, R. P. Reed, R. E. Schramm and L. L. Sparks all helped with valuable discussions of their work. P. Michals provided a great deal of assistance in retrieving and plotting the data presented here.

Table 1
Summary of Properties and Materials Treated in the References

	LOW TEMPERATURE PHYSICAL PROPERTIES								LOW TEMPERATURE MECHANICAL PROPERTIES							
	Thermal Expansion	Thermal Conductivity	Specific Heat and Enthalpy	Kapitza Resistance	Diffusivity	Lorenz Ratio	Electrical Resistivity	Dielectric Properties	Yield Strength	Notch Tensile Strength	Fracture Toughness	Stress Strain	Modulus of Elasticity	Impact Strength	Creep	Fatigue Strength
Technical Alloys: Ferrous	3, 4, 6, 48, 49, 55	10, 17, 18, 48, 49, 55	16, 49, 55		18, 49, 55	43	31, 49		48, 49	48, 49, 55	48	48, 49	48, 49, 55	48, 49, 55		48, 49
Technical Metals and Alloys: Non-Ferrous	3, 4, 6, 17, 48, 49, 55	10, 17, 18, 26, 48, 49, 55	16, 17, 49, 55		18, 49, 55	43	26, 31, 48, 49, 55		48, 49, 50	48, 49, 55	48, 55	48, 49, 55	48, 49, 50, 55	48, 49, 50, 55		48, 49, 50
Elements	3, 17	10, 17, 18	16, 17, 18	27	18	43	28, 29, 30, 32		51			51	51			51
Plastics	3, 8, 45, 48	8, 10, 17	8, 16, 17		8			8	8, 45, 48, 49		8	8, 45, 49	45, 48, 49	8, 48, 49		45
Composites: Metal Matrix																
Composites: Nonmetal Matrix	45								45			45, 48	45, 48			45, 48
Glasses and/or Quartz	3	10, 17	16, 17													
Epoxies	7, 45											45				45
Greases		10														
Varnishes		10	16, 17													
Solders	3	10	16													
Graphites and/or Ceramics	3, 6, 17, 49	10, 17, 49	16, 17, 49	27								49				

IX. References

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