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Variations of thermal conductivity with temperature and composition of Zn in the Bi–[x] at.% Zn–2 at.% Al alloys

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ABSTRACT

The variations of thermal conductivity with temperature for Bi–[x] at.% Zn–2 at.% Al alloys ($x = 4.5$, 18.0, 30.1, 79.0 and 98) were measured by using a radial heat flow apparatus. From the graphs of thermal conductivity versus temperature, the thermal conductivity of solid phases at their melting temperature for Bi–[x] at.% Zn–2 at.% Al alloys ($x = 4.5$, 18.0, 30.1, 79.0 and 98) were obtained. Dependency of the thermal conductivity on composition of Zn in the Al–Bi–Zn alloys was also investigated. According to present experimental results, the thermal conductivity of the Bi–[x] at.% Zn–2 at.% Al alloys linearly decrease with increasing the temperature and exponentially increase with increasing the composition of Zn.

1. Introduction

In the experimental determination of the thermal conductivity of solids, a number of different methods of measurement are required for different ranges of temperature and for various classes of materials having different ranges of thermal conductivity values. Many attempts have been made to determine the thermal conductivity values of solid and liquid phases in various materials by using different methods. One of the common techniques for measuring the thermal conductivity of solids is the radial heat flow method. The radial heat flow method is a steady state method and the classification is mainly based upon the specimen geometry: cylindrical or spherical. For example, the cylindrical heat flow method uses a specimen in the form of a right circular cylinder with a coaxial central hole that contains either a heater or a sink depending on whether the described heat flow direction is to be radially outward or inward [1]. The temperatures within the specimen are measured by thermocouples. This method has been widely used for measuring the thermal conductivity of solids for pure materials and alloys [2–13].

Heat in solids is conducted by various carriers: electrons, lattice waves (or phonons), magnetic excitations, and, in some cases, electromagnetic radiation. The total thermal conductivity is additively composed of contributions from each type of carrier. It can be shown that:

$$K = \frac{1}{3}\sum_{j} C_j\, v_j\, l_j \tag{1}$$

where the subscript j denotes the type of carrier. C_j is the contribution of carriers of type j to the specific heat per unit volume, v_j is the velocity of the carrier (we regard the carrier as a particle; if the carrier is a wave, the appropriate velocity is the group velocity), and l_j is a suitably defined mean free path.

The occurrence of a mean free path in Eq. (1) opens up the possibility that in some cases one cannot uniquely define the thermal conductivity of a material. This happens whenever a carrier mean free path becomes comparable to the smallest external dimension of the specimen. It happens particularly in insulators at low temperatures, because of long phonon mean free paths, and in transparent solids at high temperatures, where photons contribute significantly to heat transport. In metals it is a relatively rare occurrence, to be considered only in the case of very small particles, very thin wires, or superconductors at extremely low temperatures.

The principal carriers of heat in metals are electrons and lattice waves, leading to an overall thermal conductivity:

$$K = K_e + K_g \tag{2}$$

where K_e is the electronic component and K_g is the lattice component.

Generally K_g of metals, alloys, and semimetals is of magnitude comparable to the lattice thermal conductivity of insulators of

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corresponding elastic properties, except at low temperatures (where phonon–electron interaction reduces K_g in metals). The relative importance of K_e and K_g thus depends on the magnitude of K_e. The electronic component often parallels the electrical conductivity (Wiedemann–Franz law), and the electrical conductivity is highest in pure metals, reduced in the case of alloys, and even lower in semimetals and semiconductors.

As we consider materials of increasingly poorer conductivity, K_e becomes less important relative to K_g. In semimetals and degenerate semiconductors K_g and K_e are frequently comparable except at low temperatures, where K_e is small. In most semiconductors the electronic thermal conductivity has to be considered only at elevated temperatures.

Since K_e and K_g behave differently as functions of temperature and with the introduction of imperfections, it is important to know the relative roles of these two carriers if predictions are to be made; unfortunately, it is not always easy to know what fraction of the measured thermal conductivity can be ascribed to each.

In metals, where the density of electrons is high, the electron gas is highly degenerate, that is, all electron states of energy $E < E_f$ are filled, E_f being the Fermi energy, all states of $E > E_f$ are empty, and all conduction properties occur in an energy interval $E_f \pm 0$ $(k_B T)$, where $k_B T \ll E_f$. Under these circumstances the electronic component of the specific heat $C_e \alpha T$, ν_e is typically 10^8 cm s^{-1} and independent of temperature. Thus,

$$K_e = \frac{1}{3} C_e \, \nu_e \, l_e \propto T l_e \tag{3}$$

and its temperature dependence is governed by the temperature dependence of l_e.

Now the electron mean free path l_e also determines the electrical conductivity. Theories of the electron mean free paths are thus at the same time theories of the electrical conductivity a of metals, while the thermal and the electrical conductivity are related by the Wiedemann–Franz–Lorenz law

$$\frac{K}{\sigma T} = L_0 = \frac{1}{3}\pi^2 \left(\frac{k_B}{e}\right)^2 \tag{4}$$

where e is the electronic charge. In practical units the Lorenz number L_0 is 2.443×10^{-8} V^2 K^{-2}.

The electron mean free path is limited both by electron scattering by defects (chemical impurities and physical defects) and by the thermal vibrations; for in a perfectly periodic crystal lattice l_e would be infinite. To the extent to which the scattering rates due to different processes are additive,

$$\frac{1}{l_e} = \frac{1}{l_0} + \frac{1}{l_i(T)} \tag{5}$$

where l_0 is the residual mean free path and $l_i(T)$ the intrinsic mean free path. The first term on the right hand side of Eq. (5) describes scattering of electrons by defects, and varies from specimen to specimen, but is independent of temperature as long as the nature and concentration of defects are not functions of temperature. The second term describes scattering of electrons by lattice vibrations and varies with temperature. In the simple case when the electron gas is isotropic, i.e. the velocity and apparent density of electrons do not depend upon direction relative to the crystal axes, Eq. (5) leads to an additivity of the corresponding electrical and electronic thermal resistivities, i.e.

$$\frac{1}{\sigma} = \rho_0 + \rho_i(T) \tag{6}$$

and

$$\frac{1}{K_e} = W_e = W_0 + W_i \tag{7}$$

Here ρ_0 is the residual electrical resistivity, varying from specimen to specimen, $\rho_i(T)$ the intrinsic electrical resistivity, and W_0 and W_i are corresponding components of the thermal resistivity.

The thermal vibrations of solids contribute to the thermal conductivity. In insulators this is the only mechanism of heat transport except at elevated temperatures. The lattice thermal conductivity of metals is governed by the same theoretical considerations, but a number of cases which occur in insulators are not relevant to metals, so that the present discussion is not as comprehensive.

The thermal vibrations of a perfect crystal are described in terms of lattice waves which occupy a spectrum of frequencies from the lowest frequencies to some upper limit, ν_m of the order of 10^{13} Hz. At low frequencies these waves are identical to the elastic waves in the corresponding elastic continuum; at the higher frequencies the atomic structure of the crystal lattice leads to dispersion effects. The corresponding wavelengths range from long waves down to waves of length comparable to the interatomic distances.

These waves are randomly excited in thermal equilibrium and the energy content of the solid is given in terms of the laws of statistical mechanics. The specific heat of solids varies as T^3 at the lowest temperatures and is independent of temperature in the high-temperature regime $(T > (h\nu_m/k_B))$.

With at least two types of carriers responsible for heat transport, and with each of them being limited by several possible mechanisms, thermal conductivity in metals and alloys show a wide range of differing behavior.

The thermal conductivity of semimetals is understood in principle, but in practice we do not always have enough information to interpret it. There are two practical complications: (1) the electronic and lattice components are comparable and (2) the electronic component does not follow the Wiedemann–Franz–Lorenz law except at low temperatures.

Lead has been widely used in all aspects of life for thousands of years. It has been widely used in modern society, also, particularly in microelectronics and presents the base of majority solders up to now. But, this metal is highly toxic and therefore, it should be removed from different materials, especially electronic materials. So, the currently used lead-based solders in microelectronics are under way to be replaced by lead-free alloys due to environmental and health concerns. In that purpose, various physical, chemical and mechanical properties of the candidate alloy, as well as the economic aspect have been considered. In recent years, the development of lead-free solders for electronic interconnection materials used in electronic devices has received great attention because of the health and environmental safety problems posed by conventional Pb–Sn solders, although such solders also have favorable properties [14–17]. The Al–Bi–Zn investigated solder alloys [18] are already in practice, but only in exactly determined conditions. Considering these, it could be expected that Al–Bi–Zn ternary system might be one among proper substitutes for common solders.

Thermal conductivity (K) is the main fundamental property of materials such as density, melting point, entropy, enthalpy, resistance, and crystal structure parameters. Although the values of K for pure metallic materials were obtained theoretically and experimentally, there are not enough information and data available about the thermal conductivity of metallic alloys. The values of K for alloys change, as in pure materials, not only with temperature but also it changes by compositions of alloys. Recently, we have embarked on research pertaining to the measurement of thermal conductivity variation with temperature of multi components metallic alloys. So attention is given to the thermal and electrical conductivities at high temperature required as input data in heat transfer and solidification simulations. Thermodynamic characteristics and phase equilibrium for the Al–Bi–Zn system have been reported [18]. The variation of thermal conductivity with