34. I. E. Hill and A. L. Ruoff, "Temperature dependence of the velocity of sound in some liquid metals and eutectic alloys," Chem. Phys., 43, 2150-2151 (1965).

35. M. B. Gitis and I. G. Mikhailov, "On the relationship between the velocity of sound and electrical conductivity in liquid metals," Akust. Zh., 12, No. 1, 17-21 (1966).

36. N. F. Otpushchennikov and G. V. Konyuchenko, Acoustic Measurements of the Thermophysical and Thermodynamic Properties of Liquid Metals. Ultrasound and the Physicochemical Properties of Substances [in Russian], Kursk State Polytechnic Inst. (1971), pp. 193-197.

37. A.-M. A. Magomedov and B. P. Pashaev, "Measurement of the velocity of ultrasound in In—Sn, Bi—Cd, and Bi—Sb alloys during melting," Teplofiz. Vys. Temp., 9, No. 4, 746-750 (1971).

38. N. B. Kazakov, A. A. Pronin, and S. I. Filippov, "Acoustic studies of liquid alloys," Izv. Vyssh. Uchebn. Zaved., Chern. Metall., 9, No. 5, 8-11 (1965).

39. A. E. Vol and I. K. Kagan, "Indium—thallium," in: Structure and Properties of Binary Metallic Systems [in Russian], Vol. 3, Nauka, Moscow (1976), pp. 494-507.

40. Yu. K. Titova, S. I. Drakin, and I. B. Alikina, "Electrical diffusion in indium alloys," Zh. Fiz. Khim., 42, No. 9, 2257-2261 (1968).

41. D. K. Belashchenko, E. I. Gushchina, and K. D. Omarova, "Electron transfer and electronic properties of liquid binary metallic systems Hg—Tl and Tl—In," Fiz. Met. Metalloved., 31, No. 5, 930-938 (1971).

42. M. Hansen and K. Anderko, Structure of Binary Alloys [Russian translation], Vol. 2, Metallurgizdat, Moscow (1962).

43. Selected Values of the Thermodynamic Properties of Binary Alloys, New York—London (1973), p. 1435.

44. D. K. Palchaev, B. P. Pashaev, and V. G. Revelis, "Density of metals and alloys of the indium—tin system during melting," in: Summary of Scientific Reports of the Third International Conference on the Structure and Properties of Metallic and Slag Melts, Pt. 2, Sverdlovsk (1978), pp. 90-93.

INFLUENCE OF QUASILOCAL OSCILLATIONS ON THE THERMAL EXPANSION

AND SPECIFIC HEAT OF METALS AT LOW TEMPERATURES

L. B. Iliev, V. I. Ovcharenko,   UDC 536.631
V. P. Popov, and V. A. Pervakov

The influence of heavy impurity atoms on the thermal expansion and specific heat of magnesium, aluminum, and titanium (4-300°K) is studied. The possibility of predicting the mentioned thermophysical properties of such systems is examined.

An important problem of modern material science is the prediction of the thermophysical properties of structural materials and the development of appropriate technological recommendations. In a number of cases such predictions can be made for weak solid solutions on the basis of modern conceptions of the role of the mass of foreign atoms and of the perturbations of interatomic binding forces. Systems with heavy impurity atoms are of interest since an anomalously high rise in the specific heat and thermal expansion can be observed in this case at low temperatures [1-7] because of the occurrence of quasilocal vibrations (QLV). Such impurities are often contained in light metals and alloys used in cryogenic engineering, which stimulates the study of the thermophysical properties of similar systems. Unfortunately, the known literature data for many engineering alloys cannot be compared to computations because of their poor accuracy, and therefore, cannot be analyzed from the viewpoint mentioned; specially designed experiments are needed.

The influence of heavy impurity atoms resulting in the occurrence of QLV on the specific heat and thermal expansion of light metals such as magnesium, aluminum, and titanium is studied in this paper. The problem of obtaining experimental results and comparing them to results of theoretical computations to clarify the possibility, in principle, of predicting
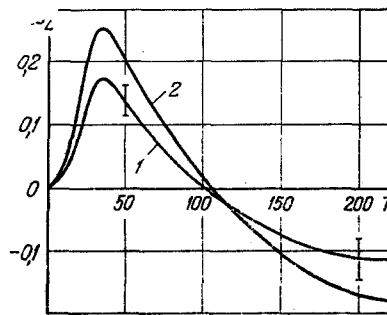
Fig. 1. Changes in the lattice specific heat of magnesium due to a lead impurity: 1) 0.9 at. % Pb; 2) 1.4 at. % Pb. ΔC_L, J/ mole·°K; T, °K.

the temperature dependences of the mentioned thermophysical characteristics of such systems, which is needed for applied purposes, is posed.

Solid solutions of Pb and Cd in magnesium, Cu, Ag, Au, and Pb in aluminum, and Sn in titanium were investigated. Because of the slight solubility, the Au and Pb concentrations in aluminum were comparatively low (0.08 and 0.15 at. %, respectively) while in the other cases the impurity concentrations varied around 1 at. %. A more complex solid solution Ti + 9.4 at. % Al + 1.0 at. % Sn (the alloy VT5-1) was also investigated, where the total effect is a result of superposing contributions of both heavy (Sn) and light (Al) impurities. For the comparison, the influence of the light impurity was examined separately in an example of the alloy Ti + 8.6 at. % Al (VT5).

Other authors have studied the influence of QLV on just the specific heat (where certain of the systems we studied were also examined, viz., Mg–Pb [8,9], Mg–Cd [9], Al–Ag [10]); however, the investigations were conducted in all cases in a narrow temperature range ($\leqslant$25-30°K). The specific heat and thermal expansion were studied mainly in the 4-300°K range in our research.

A standard vacuum adiabatic calorimeter was used to measure the specific heat. The characteristic components of the apparatus are described in [11,12]. The measurement accuracy in the low-temperature section (<30°K) was ±(0.5-1)% and ±(0.1-0.2)% at the higher temperatures. The thermal expansion was measured by using two (computed at different temperature ranges) differential dilatometers described earlier [13]. The maximal resolution in determining the difference in the thermal linear expansion coefficient (TLEC) reached ±0.5·10^{-8} °K^{-1}, which permitted determining the values of the TLEC for the alloys being investigated to ±(1-2)% accuracy below 30°K, ±(0.5-1)% in the 30-80°K range, and ±0.2% for higher temperatures.

Magnesium Alloys. The temperature dependences we obtained for the increment in lattice specific heat due to the lead impurity in magnesium ($\Delta C_L = C_{L(Mg-Pb)} - C_{L(Mg)}$; $m_{Pb}/m_{Mg} = 8.5$) are shown in Fig. 1. A rise in the lattice specific heat, which agrees in magnitude with the results in [9], is observed with the rise in temperature in the low-temperature section (for which there are literature data (T $\leqslant$ 25°K)). For 35°K the curves have a maximum, while for T $\geqslant$ 100°K they pass below the horizontal axis.

Such a nature of the curves was predicted for a broad temperature range in theoretical research. The impurity growth of the specific heat is due to the occurrence of a quasilocal peak in the vibrational spectrum [1-4]. The maximum is associated with the fact that the molar specific heat should, in the long run, approach the classical limit (to the accuracy of anharmonic effects) for sufficiently high temperatures (T >θ). In the intermediate domain a change in the sign of ΔC can be observed which is due to the fact that the states density in the spectrum to the right of the quasilocal peak is lower than in the case of a pure metal with an unperturbed spectrum [2,5]. A computed curve is presented in [2] for the increment in the specific heat of a system with parameters similar to those in the case under consideration. Good qualitative agreement with the results of our experiment is observed. The quantitative estimates naturally differ somewhat, but are of the same order as those we obtained.

The computation was performed for a fcc lattice with a $m'/m = 9$ relationship between the mass of the impurity and majority atoms. The real specimen had a hexagonal lattice and the mass relationship $m_{Pb}/m_{Mg} = 8.53$. The computation was performed without taking account of the perturbations of the force constants although according to [14] a certain attenuation in the interatomic bonds could be expected in this case. Nevertheless, the computational data presented predict the behavior of the temperature dependence of the specific heat of the alloy with a $\leqslant 3\%$ error in the 30–80°K band and $\lesssim 1\%$ at higher temperatures. A more accurate computation requires taking account of perturbations in the force constants, and possibly, additional information on the reconstruction of the phonon spectrum.

There are computational data for the low-temperature domain which take more fully into account the different aspects of impurity perturbation [3, 4]. The relative rise in the specific heat in this section reaches the highest values. It is 50% (converted to 1 at. % of the Pb impurity) at the maximum point (T = 11–12°K). The computed values agree with the experimental (within the error limits) if attenuation of the interatomic bonds between the nearest neighbors to the impurity reaches $\approx 15\%$. Lower magnitudes are obtained without taking this circumstance into account; in particular, the computed value of $\Delta C/C$ reaches 43% at the maximum point.

Analogous measurements were also executed for the Mg–Cd system $(m_{Cd}/m_{Mg} = 4.6)$. The results are qualitatively similar to those presented above in the low-temperature section. However, changes in the sign of ΔC are not observed at elevated temperatures — the changes in specific heat are lost in the errors in the experiment $(|\Delta C/C| \leqslant 0.2\%)$.

Therefore, heavy impurities $(m'/m \leqslant 9)$ result in a noticeable rise in the specific heat (to 50% per 1 at. % impurity) of magnesium at low temperatures $(\leqslant 30°K)$. For a weak perturbation of the force constants in the area of the impurity atoms $(\leqslant 20\%)$, the specific heat of the system with an impurity can be computed to the accuracy on the order of percents $(\leqslant 10\%)$ with just the difference between the masses of the impurity and majority atoms taken into account. More accurate predictions (to ±1%) are possible with the change in the interatomic binding forces taken into account, where they can be estimated from data for the elastic moduli in the temperature range under consideration. Above 30°K, the impurity increment in the specific heat is comparatively small (<10%); hence, for a weak perturbation of the force constants the temperature dependence of the specific heat can be computed with satisfactory accuracy with the difference between just the corresponding atomic masses taken into account $(\lesssim 3\%$ in the 30–80°K band and $\leqslant 1\%$ at higher temperatures). Taking account of the perturbation in the force constants should, in principle, yield a better approximation; however, computational data for this temperature range are not known in the literature.

The temperature dependences of TLEC increments (lattice part) are similar for $T \leqslant 30°K$ to the dependences $\Delta C_L(T)$. The relative values of the corresponding increments agree within the limits of error. Therefore, the behavior of the TLEC of this alloy can be described by the known Gruneisen relationship

$$\alpha = \gamma \frac{\varkappa}{3V} C$$

with approximately the same values of the parameter γ and the compressibility factor $\varkappa$ as for the pure metal. This latter is the result of the slight change in the compressibility of magnesium upon the insertion of 1 at. % of the impurity Pb at low temperatures (according to the estimate obtained above, the perturbations of the interatomic bonds are less than 1%). This contribution can be neglected in this temperature band since the specific heat here varies by tens of percents.

For T > 30°K the nature of the temperature dependences ΔC_L and $\Delta \alpha_L$ differ, where $\Delta \alpha_L(T)$ again starts to grow with the rise in temperature, after a certain tendency to saturation. The further history of this curve is shown in Fig. 2. No change in sign is observed (as for ΔC). However, a slight diminution with the rise in temperature starts at $\approx 100°K$. For T 100°K (increment in specific heat is $\Delta C_L \approx 0$), the relative change in α_L is (if the mean over two curves is taken) 1.6% per 1 at. % impurity, which almost agrees with the value of the relative change in compressibility at room temperature [14].

Therefore, the singularity in the behavior of the curves $\Delta \alpha_L$ in this temperature domain can be interpreted as the appearance of the predominant contribution to the change in compressibility. The reduction in $\Delta \alpha_L$ with the rise in T after 100°K corresponds to the temperature history of the increment in the specific heat.
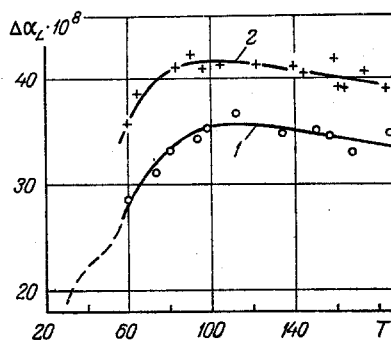
Fig. 2.

Fig. 3.

Fig. 2. Change in the lattice part of TLEC of magnesium due to the lead impurity: 1) 1.36 at. % Pb; 2) 1.83 at. % Pb, $\Delta\alpha_L \cdot 10^8$, °K^{-1}.
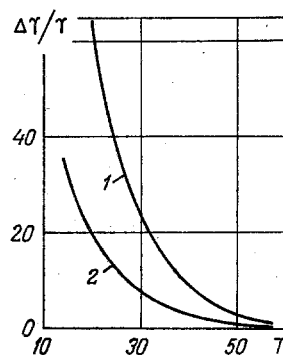
Fig. 3. Relative changes in the Gruneisen parameter γ due to the impurity Pb (1) and Ag (2) in aluminum (converted per 1 at. %), $\Delta\gamma/\gamma$, %.

Thus, the temperature dependence of $\Delta\alpha$ can be determined in the whole temperature range by the relative changes in the specific heat and compressibility due to the impurity ($\Delta\alpha/\alpha = \Delta C/C + \Delta\varkappa/\varkappa$). The Gruneisen parameter γ remains unchanged in this case

In the case of the Mg–Cd system the behavior of $\Delta\alpha$ is determined completely by the temperature dependence of the specific heat since the perturbation of the elastic moduli is insignificant for this system [14].

Therefore, the temperature dependence of the TLEC can be computed on the basis of the Gruneisen relationship for magnesium with heavy impurity atoms weakly perturbing the force constants, by means of known data for the specific heat and the elastic moduli. The Gruneisen parameter here can be considered the same as for the pure metal. The accuracy of the computation depends on the accuracy with which the values of the initial parameters are known. Taking account of the error in our experiment, it can be considered that the method used allows a prediction accuracy of $\pm(1-2)$% in the temperature band $\leqslant 80$°K and ± 0.5% for higher temperatures, in the optimal variant.

Aluminum Alloys. The general nature of the temperature dependences of the specific heat increments due to the impurity atoms is identical in all cases: initially ΔC increases with the rise in temperature, passes through a maximum, and then approaches zero. Values of ΔC correspond to the computed ones, obtained taking account of both the difference in the masses and the perturbations of the force constants. Sign changes were not observed successfully at elevated temperatures since systems with quite definite QLV (whereupon the appearance of the effect could be expected) contained low-impurity atom concentrations, in which connection the appropriate changes in the specific heat were within the limits of experiment error.

Analysis of the possibility of predicting the temperature dependences of the specific heat of impurity systems based on aluminum results in the same deductions as in the case of magnesium alloys. A sufficiently high accuracy of prediction can be achieved only when the perturbation of the interatomic bond is taken correctly into account.

The behavior of the temperature dependences of the TLEC increment is qualitatively similar to that observed in the case of the magnesium alloys. However, quantitative estimates cannot be made at low temperatures on the basis of data of just the specific heat and compressibility; relative changes in the TLEC noticeably exceed the total contribution of the relative changes in these quantities ($\Delta\alpha/\alpha > \Delta C/C + \Delta\varkappa/\varkappa$). As the temperature is lowered, this discrepancy grows, where the effect is more strongly manifest in systems with heavier impurity atoms.

Such a difference indicates a change in the Gruneisen parameter due to an impurity. Curves of $\Delta\gamma/\gamma$ as a function of T are presented in Fig. 3 as constructed from our data for certain systems. The effect can be explained as follows. In contrast to magnesium, the growth
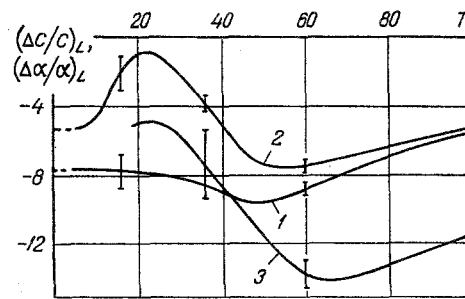
Fig. 4. Relative differences in the
specific heat and TLEC of titanium
alloys and of pure titanium: $(\Delta C/C)_L$:
1) for VT5; 2) VT5-1; $(\Delta\alpha/\alpha)_L$: 3) VT5-1.
$(\Delta C/C)_L$, %; $(\Delta\alpha/\alpha)_L$, %.

of γ is observed in aluminum with the reduction in the temperature [15]. If γ is considered as the averaged value of Gruneisen parameters γ_i of individual modes [15], then its rise with the reduction in T can be treated as the result of the fact that γ_i have greater values at the low-frequency section of the spectrum than in the high-frequency band. In the presence of QLV the states density of the low-frequency vibrations is high, which results in an additional increase in the average γ as the temperature is reduced. The effect is hence naturally more definite in systems with a more perturbed spectrum, i.e., with heavier impurity atoms.

The effect mentioned makes application of the Gruneisen relationship difficult for computations since it requires additional information on the anharmonic properties of the crystal. It is not excluded that the behavior of the Gruneisen parameter will be still more complicated in the case of impurities which perturb the interatomic binding constants strongly (to $\approx 100\%$).

Therefore, the applicability criterion for the computation method under consideration can be considered to be the independence of the Gruneisen parameter of a pure metal from the temperature for systems with heavy impurity atoms perturbing the force constants weakly.

Titanium Alloys. The temperature dependence of the increment in the lattice specific heat due to a tin impurity (0.82 at. %) in titanium is obtained. The effect is in good agreement with the computed data [4], taking account of both the difference in the masses of impurity atoms and the perturbation of the force constants ($m_{Sn}/m_{Ti} = 2.5$, attenuation of the force constants in the area of the impurity atoms is $\approx 30\%$).

The appearance of the effect mentioned occurs in the more complex case when an impurity of a different species which does not result in the occurrence of QLV is also present in addition to the heavy impurity atoms. This case is illustrated by the example of the Ti—Al—Sn alloy. Relative changes in the specific heat due to an Al impurity (curve 1) and the Al and Sn impurities jointly (2) in titanium are shown in Fig. 4.

The phonon components of the alloy specific heats are below the corresponding values for titanium in the whole temperature range. The diminution in the specific heat with the dissolution of the aluminum can be observed in connection with the low mass of the foreign atoms ($m_{Al}/m_{Ti} = 0.56$) and the magnification of the interatomic binding forces. Both these factors result in a diminution in the density of the low-frequency modes, which also results in a reduction in the specific heat at low temperatures [2-4]. The behavior of the specific heat in the more complex alloy VT5-1 can be explained as the result of superposition of two effects, the contribution of the Al impurity, which reduces the specific heat, and the contribution of the heavier impurity Sn, resulting in a growth of the phonon specific heat in the low-temperature section. The relative values of the contribution of the impurity Sn are in good agreement with the data for the Ti—Sn alloy. Converted to an identical concentration, the contributions of the Sn impurity agree within the limits of experimental error in binary and more complex alloys.

The thermal expansion was investigated only in the alloy VT5-1. The temperature dependence of the difference in TLEC of the alloy and titanium is similar to the analogous curve for the difference in the specific heats (Fig. 4), and therefore, in conformity with the Gruneisen relationship, the behavior of this dependence can be explained mainly by the

appearance of the same factors as in the specific heat case. However, an appropriate computation should be performed taking account of both changes in compressibility and changes in the Gruneisen parameter.

It should be noted that because of the strong anisotropy, the thermal expansion of titanium and its alloys depends noticeably on the orientation of the crystalline grains. In our case, we investigated polycrystalline specimens known to be untextured, which were inspected by x-ray diffraction.

NOTATION

C, molar specific heat; α, coefficient of linear thermal expansion; γ, Gruneisen parameter; $\varkappa$, coefficient of isothermal compressibility; V, molar volume; T, absolute temperature; Θ, Debye temperature; m, atomic mass.

LITERATURE CITED

1. Yu. M. Kagan and Ya. V. Iosilevskii, "On the anomalous behavior of the specific heat of crystals with heavy impurity atoms," Zh. Eksp. Teor. Fiz., 45, No. 3 (9), 819-821 (1963).
2. A. Maradudin, Defects and the Vibrational Spectrum of Crystals [Russian translation], Mir, Moscow (1968), pp. 66-83.
3. A. P. Zhernov and G. R. Augst, "On the influence of changes in the force constants on the properties of crystals with impurity atoms," Fiz. Tverd. Tela, 9, No. 8, 2196-2205 (1967).
4. V. I. Peresada and V. P. Tolstoluzhskii, "Low-temperature specific heat of a fcc lattice containing a substitution impurity," Fiz. Nizk. Temp., 3, No. 6, 788-800 (1977).
5. Ya. A. Iosilevskii, "On the thermal equation of state of solid solutions," Fiz. Tverd. Tela, 9, 2661-2669 (1967).
6. V. P. Popov and V. A. Pervakov, "Thermal expansion of dilute solid solutions of silver in aluminium at low temperatures," Phys. Status Solidi (b), 71, K95-K97 (1975).
7. V. P. Popov and V. A. Pervakov, "Thermal expansion of magnesium with a lead impurity at low temperatures," Fiz. Tverd. Tela, 17, 2799-2800 (1975).
8. R. Kh. Panova and Samoilov, "Experimental detection of the anomaly in the specific heat of a metal with heavy impurity atoms," Zh. Eksp Teor. Fiz., 49, No. 2 (8), 456-458 (1965).
9. J. A. Cape, G. W. Lehmann, W. V. Johnston, and R. E. De Wames, "Calorimetric observation of virtual bound-mode phonon states in dilute Mg–Pb and Mg–Cd alloys," Phys. Rev. Lett., 16, No. 20, 892-895 (1966).
10. W. M. Hartmann, H. V. Culbert, and R. P. Huebener, "Enhancement of lattice heat capacity due to low-frequency resonance modes in dilute aluminium–silver alloys," Phys. Rev., B1, No. 4, 1486-1493 (1970).
11. G. A. Zaitsev, V. I. Ovcharenko, and V. I. Khotkevich, "Use of carbon adsorption pump in an adiabatic vacuum calorimeter for 4.2-300°K temperatures," Prib. Tekh. Eksp., No. 1, 212 (1967).
12. V. I. Ovcharenko, G. A. Zaitsev, V. S. Krylovskii, V. A. Pervakov, and V. I. Khotkevich, "Specific heat of a niobium alloy with molybdenum (type VN-2) at low temperatures," in: Thermophysical Properties of Substances at Low Temperature [in Russian], VNIIFTRI, Moscow (1972), pp. 117-120.
13a. V. P. Popov and V. A. Pervakov, "Precision measurement of small temperature coefficient of linear expansion differences," Izm. Tekh., No. 12, 48-49 (1978).
13b. V. P. Popov and V. I. Khotkevich, "Differential quartz dilatometer for solid state investigation in the 60-373°K temperature range," Abstracts, First All-Union Conf. "Methods and Instruments for Accurate Dilatometer Investigations," VNIIM, Leningrad (1973), p. 67.
14. D. Hardie, "The elastic properties of magnesium solid solutions," Acta Met. 19, No. 7, 719-723 (1971).
15. S. I. Novikova, Thermal Expansion of Solids [in Russian], Nauka, Moscow (1974), pp. 12-15.