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Relaxation Phenomena Caused by Equilibration of Point Defects

Y. Kraftmakher[1]

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Relaxation phenomena due to equilibration of point defects in metals are reviewed. The relaxation effect in specific heat observed in tungsten and platinum confirms that in both cases the nonlinear increase in the high-temperature specific heat has to be attributed to point-defect formation. Relaxation phenomena observed by measurements of electrical resistivity and positron annihilation are also considered. The comparison of the data seems to be favorable for the conclusion that all the phenomena are of one origin.

KEY WORDS: electrical resistivity; high temperatures; modulation calorimetry; point defects in metals; relaxation phenomena; specific heat.

1. INTRODUCTION

The strong nonlinear increase in specific heat and thermal expansivity of metals at high temperatures is well established. A natural explanation of this phenomenon is the formation of point defects in the crystal lattice. However, in many cases the equilibrium concentrations of the defects deduced from the nonlinear contributions are of the order of 1% at melting points [1].

The point-defect formation in solids was predicted by Frenkel [2]. At high temperatures, some atoms get energies sufficient enough to leave their positions in the lattice and to occupy interstitial positions. In this case, a vacancy and an interstitial (Frenkel pair) appear simultaneously. A way to create only vacancies was shown later [3]: Atoms leave their lattice positions and occupy free positions on a surface or at internal imperfections (voids, grain boundaries, dislocations). Point defects are

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[1] The Jack and Pearl Resnick Institute of Advanced Technology, Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel.

thermodynamically stable because they enhance the entropy of the crystal. The equilibrium vacancy concentration is

$$c_v = \exp(S_F/k_B)\exp(-H_F/k_B T) = A\exp(-H_F/k_B T) \qquad (1)$$

where H_F is the enthalpy of formation, S_F is the entropy of formation (not including the configurational entropy), k_B is the Boltzmann constant, and T is the absolute temperature. Usually, the enthalpies of vacancy formation obtained with various methods are in good agreement. However, there are significant differences in the entropies of formation.

Experimental methods of studying point defects in metals may be divided into three groups.

(1) Defects in equilibrium are studied through physical properties of metals: specific heat, thermal expansion, electrical resistivity, thermopower, positron annihilation. However, properties of a hypothetical defect-free crystal cannot be calculated accurately. It is therefore impossible to separate reliably the defect contributions.

(2) Samples are studied in which point defects are created by quenching, deformation, of irradiation. The main disadvantage of equilibrium measurements is completely excluded here because samples with extra point defects are compared with well-annealed samples in which defect concentrations are negligible. However, the obtained extra concentrations are smaller than equilibrium concentrations of the defects at high temperatures.

(3) For relaxation measurements, properties of samples at high temperatures are studied at such rapid changes of temperature that the defect concentration cannot follow them. Under such conditions, the influence of the defects is almost completely excluded and values are measured corresponding to a defect-free crystal. This relates only to properties that depend on changes of the defect concentrations during the measurements: specific heat, thermal expansivity, and temperature derivative of electrical resistivity. If the defect concentration does not follow the temperature and retains a mean value, then these properties practically correspond to a defect-free crystal. The relaxation technique combines the advantages of the other methods and permits an unambiguous separation of defect contributions to the physical properties.

It is recognized now that properties of equilibrium point defects are to be studied at high temperatures [4]. The relaxation measurements are very desirable for determination of the defect contributions. The criteria for choice of a suitable property are quite clear: the relative value of the defect contribution and reliability of separating it, accuracy of the measurements, and knowledge of parameters entering relations between the contributions and the concentrations of the defects. The most suitable property is the specific heat because (1) the high-temperature specific heat of a defect-free crystal depends weakly on temperature; (2) as a rule, the defect contribution is much larger than the uncertainty of the measurements; (3) the concentration can be immediately deduced from the defect contribution; and (4) measurements of specific heat at rapid changes of the temperature are simpler than similar measurements of other properties.

2. THE RELAXATION PHENOMENON IN SPECIFIC HEAT

Modulation calorimetry seems to be the most suitable technique to search for relaxation phenomena in specific heat. It is based on creating periodic oscillations of a power applied to a sample and registering oscillations of the sample temperature around a mean value (see the reviews in Refs. 5 and 6). The frequency of the temperature oscillations can be changed over a wide range. Relaxation phenomena appear when the period of the modulation becomes comparable with the characteristic time of a process contributing to the specific heat. When the specific heat of metals is measured at a sufficiently high modulation frequency, then the result corresponds to a defect-free crystal. At medium frequencies the result depends on the frequency and the relaxation time. From the complex expression for specific heat $C(X) = C + \Delta C/(1 + iX)$, one obtains [7]

$$|C(X)|^2 = (C_0^2 + C^2X^2)/(1 + X^2) \tag{2}$$

$$\tan \Delta\varphi = X\,\Delta C/(C_0 + CX^2) \tag{3}$$

Here ΔC and C are the relaxing and nonrelaxing parts of the specific heat (ΔC is the point-defect contribution), $X = \omega\tau$ is the product of the angular frequency and the relaxation time, $C_0 = C + \Delta C$ is the specific heat at $X^2 \ll 1$, and $\Delta\varphi$ is the change in the phase of the temperature oscillations. An observable relaxation effect (the difference between specific heats at low and high modulation frequencies) depends on the defect contribution to the specific heat under equilibrium and on the value of X. The temperature behavior of the effect corresponds to gradually decreasing X at increasing temperature. Hence, at a given modulation frequency, the magnitude of the effect first increases with the temperature, reaches a maximum, and then falls because of the decrease in the relaxation time. Assuming the density of sources and sinks for the defects to be constant, it is easy to evaluate the temperature dependence of the phenomenon. The quantity X obeys the expression

$$X = \exp[H_M((1/k_B T) - (1/k_B T_0))] \tag{4}$$

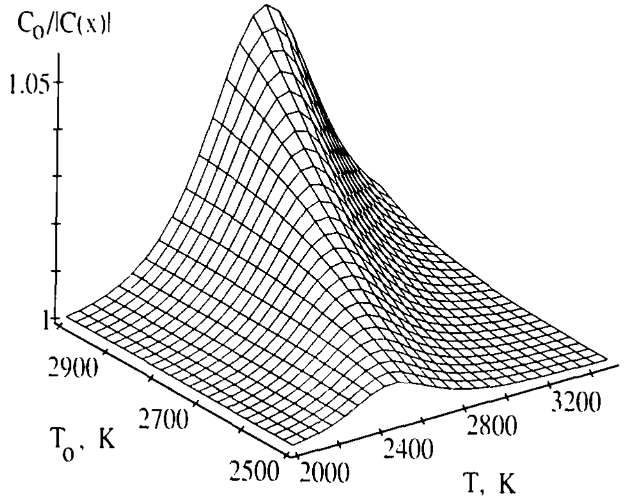

Fig. 1. Example of calculations of the relaxation effect in the specific heat of tungsten. The enthalpy of formation is assumed to be 3.15 eV [13] and the enthalpy of migration is taken to be 3 eV. T_0 is the temperature for which $X = 1$.

where H_M is the enthalpy of migration, and T_0 is a temperature for which $X = 1$ (Fig. 1).

To search for the relaxation phenomenon, a method [8] of measuring specific heat at frequencies of the order of 10^5 Hz was developed (earlier, similar measurements were performed at frequencies up to 10^3 Hz [9, 10]). A sample in the form of a thin wire or a foil was heated by a high-frequency current slightly modulated by a low frequency (Fig. 2). The high- and low-frequency temperature oscillations were therefore created in the sample simultaneously. The temperature oscillations were detected with a photomultiplier. The low-frequency component of its output signal was measured with a lock-in amplifier. The high-frequency signal was selected with a resonant circuit and measured using frequency conversion and lock-in detection. The reference voltage for the lock-in detector was provided by an auxiliary frequency converter. The voltage proportional to the difference between the amplitudes of the high- and low-frequency temperature oscillations was recorded. The measurements started at temperatures where the nonlinear increase in the specific heat was negligible and no relaxation phenomenon was expected. At these temperatures, the recorded signal was adjusted to be close to zero. Thus, at a given mean temperature, the difference between the specific heats corresponding to both frequencies was recorded immediately.

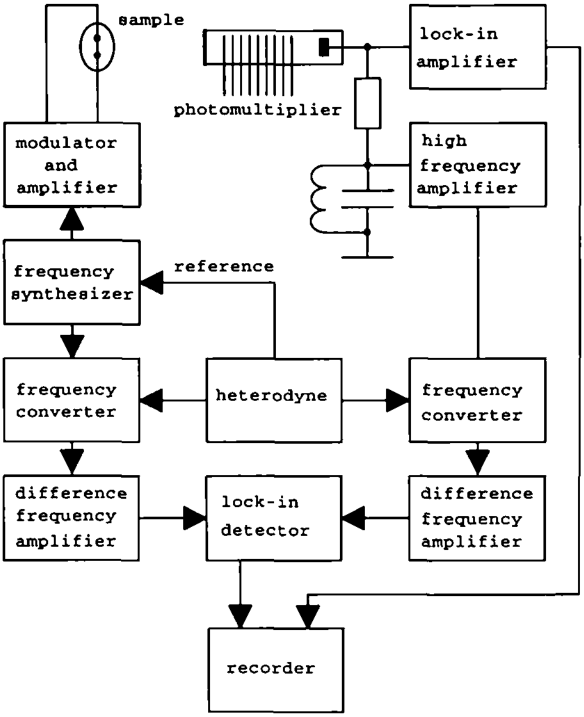

Fig. 2. Block diagram of the setup for observation of relaxation phenomena in high-temperature specific heat of metals.

The measurements were performed on wire samples of commercial tungsten 8 μm thick and on vacuum incandescent lamps with tungsten filaments 10 to 20 μm in diameter. The high frequency of the temperature oscillations was 3×10^5 Hz. The character of the temperature dependence of the effect was always within the expectation [11]. In the case of platinum, the high modulation frequency was only 5×10^4 Hz [12]. This decrease is due to the lower melting temperature. The power heating the sample and the amplitude of its oscillations become therefore much smaller which leads to a decrease in the temperature oscillations. The samples were cut from a platinum foil 10 μm thick. The temperature dependence of the relaxation effect was in a satisfactory agreement with the nonlinear increase of the specific heat. As in the case of tungsten, the scatter of the data increases in the region where X is of the order of unity, because only in this region does the relaxation effect depend strongly on X. The vacancy contribution to specific heat is [1]

$$\Delta C = (N H_F^2 A / k_B T^2) \exp(-H_F / k_B T) \tag{5}$$

where N is the Avogadro number. The enthalpies of point-defect formation in metals are nearly proportional to melting temperatures T_M, while the different equilibrium concentrations are caused by various entropies of formation. This means that the ratio of the defect contribution to the specific heat at a given temperature, ΔC, to its value at the melting point, ΔC_M, is a common function of the ratio $t = T/T_M$ for all metals:

$$\Delta C / \Delta C_M = t^{-2} \exp[B(1 - t^{-1})] \tag{6}$$

where $B = H_F / k_B T_M \simeq 9$. It was therefore possible to compare the observed relaxation effects in both metals (Fig. 3). The effect in platinum obtained at a lower frequency is observable closer to the melting point than in tungsten. This difference is probably due to a lower dislocation density in the platinum samples. The relaxation measurements thus confirm that the nonlinear increase in the specific heat of tungsten [13] and platinum [14] has to be attributed to equilibrium point defects.

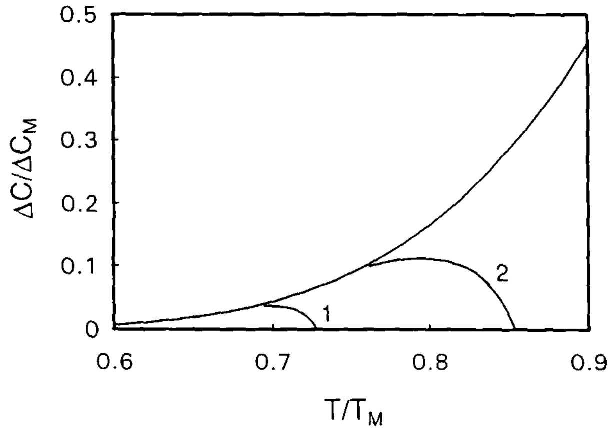

Fig. 3. Comparison of the relaxation effects in tungsten and platinum (schematically): (1) tungsten, 3×10^5 Hz [11]; (2) platinum, 5×10^4 Hz [12].

3. RELAXATION PHENOMENA IN RESISTIVITY AND POSITRON ANNIHILATION

Methods of studying equilibration of point defects were proposed long ago [15, 16]. One of the approaches is based on pulse heating of the samples and following quenching, while in another approach one supposes periodic oscillations of the sample temperature about a mean value. In first studies of vacancy equilibration, a sample under study was rapidly heated up to a given temperature, kept at this temperature for a certain time, and then quenched. The extra electrical resistivity of the sample was determined as a function of the time spent at the high temperature [17, 18]. Usually, the extra electrical resistivity is measured at low temperatures, where the main contribution is due to the frozen-in vacancies. This technique is therefore very sensitive, allowing studies of vacancy equilibration at temperatures where the relaxation times are long enough. For instance, it is easy to measure extra electrical resistivities of quenched samples which amount only to 0.001 % of the electrical resistivity at high temperatures.

Vacancy equilibration in gold was also studied by the positron annihilation technique [19]. The sample was first heated to an initial temperature. Then it was rapidly, for 0.5 ms, heated to a higher temperature. The time of exposure at this temperature was subdivided into seven intervals, and within each interval the parameters of positron annihilation, the positron lifetime and the Doppler broadening of the γ-line, were measured. Then the sample was cooled and the cycle was repeated. The necessary data were accumulated during 10^6 cycles. In the experiment, the sample temperature was rapidly changed from 500 to 600, from 680 to 800, and from 790 to 900 K. In the first case, no changes in the annihilation parameters were found, because at these temperatures the vacancy concentrations are negligible. At temperatures 800 and 900 K the relaxation times were found to be 11.7 and 3.6 ms, respectively.

There are no doubts that extra electrical resistivity of quenched samples and changes in the annihilation parameters are caused by vacancies. At the same time, many authors do not recognize a relation between the vacancy formation and the nonlinear increase of specific heat and thermal expansivity. It is therefore useful to compare results of all relaxation experiments, even for various metals (Fig. 4). The relaxation times depend also on the density of sources (sinks) for the vacancies. Hence, the differences in the relaxation times in gold obtained by electrical resistivity measurement [17] and by positron annihilation technique [19] are quite understandable. Probably, various densities of internal defects are also responsible for the difference in the relaxation times in platinum. The straight lines in the graph correspond to the equation $\tau = B \exp(H_{\mathrm{M}}/k_{\mathrm{B}}T)$, where

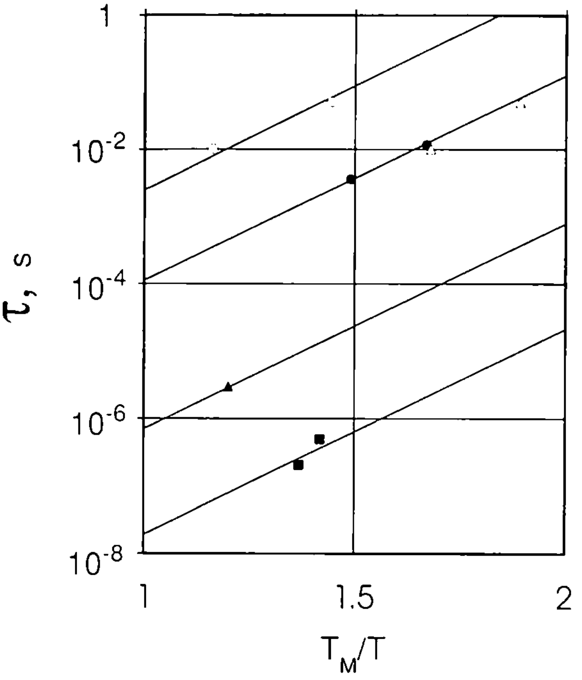

Fig. 4. Relaxation times obtained in various experiments: (○) Au, resistivity [17]; (●) Au, positron annihilation [19]; (△) Pt, resistivity [18]; (▲) Pt, specific heat [12]; (■) W, specific heat [11].

τ is the relaxation time, H_M is the migration enthalpy, and B is a preexponential factor. The enthalpies were considered to be proportional to melting temperatures ($H_M/k_B T_M = 7$). The density of sources (sinks) was assumed to be independent of the temperature. In this case, the temperature dependence of the relaxation time can be calculated from a single value. For tungsten, two relaxation times were deduced: 5×10^{-7} s at 2600 K and 2×10^{-7} s at 2700 K. The short relaxation times correspond to the well-known fact that the dislocation densities in samples of refractory metals are much higher than those in metals such as gold or platinum. The comparison of the data seems to be favorable for the conclusion that all the relaxation phenomena are of one origin.

Studies of point-defect equilibration seem to be most important for establishing reliable relations between point defects and thermophysical properties of metals. The directions of further investigations are quite clear: (1) to employ perfect samples which make it possible to observe the phenomenon over a wider temperature range and (2) to perform measurements on metals in which low dislocation densities are obtainable.

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