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Observation of Relaxation Phenomena in Thermophysical Properties of Metals[1]

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Studies of relaxation phenomena related to thermophysical properties of metals are reviewed. They provide important information not available from other techniques. Observation of relaxation phenomena was used in studying ordering in alloys, glass transition in supercooled liquids, and equilibration of point defects in a crystal lattice. Opportunities to observe the equilibration phenomena in materials are provided by subsecond thermophysical measurements. A simple method is proposed for a straightforward determination of the defect contribution to the enthalpy of metals.

KEY WORDS: glass transition; high temperatures; ordering in alloys; point defects in metals; relaxation phenomena; subsecond thermophysics.

1. INTRODUCTION

Relaxation phenomena in thermophysical properties occur after changes in temperature. Opportunities for observations of such phenomena are provided by subsecond thermophysical measurements [1–4]. Under usual conditions, temperature changes slowly, which permits establishment of equilibrium. This means that temperature changes are too slow to observe fast relaxation processes. An example of a very fast process is electron–phonon relaxation in metals. When the electrons are heated above the temperature of the lattice, the relaxation time is of the order of 10^{-12} s. However, it becomes measurable when the sample is heated rapidly. For instance, electron–phonon relaxation in a thin niobium film (about 20 nm) has been studied [5]. The electrons were excited with a laser pulse having

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a duration of the order of 10^{-13} s. Changes in the transmitted probe intensity were measured for time delays up to 1.5×10^{-12} s with respect to the pump. The probe signal depended on the lattice temperature, so that relaxation was clearly seen. In another investigation [6], the transient reflectivity and transmittivity of thin gold films were measured. The observed relaxation was interpreted as a result of thermalization of the electron gas. The thermalization time, of the order of 10^{-12} s, is thus comparable to the electron–phonon time.

On the other hand, processes are known for which relaxation times are sufficiently long to make the phenomena easily observable. Relaxation phenomena appear in diffusion-controlled processes, such as ordering in alloys and formation of point defects in the lattice of crystals. Studies of relaxation provide information not available from measurements under equilibrium conditions. First, the kinetics of the equilibration can be determined. Second, and sometimes even more important, the observations permit a reliable separation of contributions to physical properties of metals. They become distinguishable due to different relaxation times. The equilibration can be monitored through various physical properties of the sample. The simplest approach is to measure its electrical resistivity, but usually changes in the resistivity are relatively small. Observations of the relaxation in enthalpy and specific heat are important because they yield energetic characteristics of the process under study.

In this brief review, the following phenomena related to relaxation are considered: (i) ordering in alloys, (ii) glass transition in supercooled liquids, and (iii) equilibration of point defects. The main emphasis is placed on observations of the equilibration of point defects. At present, they play a major role in the determination of equilibrium concentrations of point defects and their influence on properties of metals at high temperatures. An important method of studying vacancy formation is based on rapid cooling (quenching) of the samples from high temperatures. The quenched-in vacancies become immobile at low temperatures, so that this nonequilibrium state can be held for a long time. Usually, it is monitored by measurements of the extra resistivity caused by the vacancies. The aim of quenching experiments is twofold: (i) to reveal the vacancy concentrations at high temperatures and the formation enthalpies and (ii) to determine the migration enthalpies through annealing of the quenched samples.

The methods of studying relaxation in thermophysical properties of metals may be grouped as follows.

(a) The sample is rapidly heated to a higher temperature (or cooled to a lower temperature), and the equilibration is monitored through measurements of a proper physical property of the sample, e.g., electrical resistivity, enthalpy, or the parameters of positron annihilation. This method has the advantage that both initial and final states of the sample are well defined. As a drawback, relatively small changes in the chosen property have to be measured. This technique was employed in studies of ordering in alloys [7–10] and in measurements of enthalpy related to equilibrium vacancies [11]. Also, the vacancy equilibration was studied with the positron annihilation [12]. Owing to the high sensitivity of the method, the measurements were carried out far below the melting point, so that the equilibration time was sufficiently long. With the resistivity as a probe, the measurements should be performed at higher temperatures and hence shorter relaxation times.

(b) The sample is rapidly heated to a high temperature, kept at this temperature for an adjustable time, and then quenched. Resistivity after quenching is measured and related to the time of exposure to high temperature. This method was employed in studies of the vacancy equilibration [13–15]. However, it was difficult to evaluate correctly the vacancy contribution at high temperatures. During quenching, there is sufficient time for many vacancies to be annihilated or to form clusters. When the quenched vacancies form clusters, their contribution to resistivity decreases. The extra resistivity of quenched samples becomes therefore smaller than the vacancy contribution at the high temperature. An important advantage of this approach is the high sensitivity. The extra resistivity is measured at liquid helium temperatures, where it makes the main contribution. For instance, an extra resistivity of 1 ppm of the total resistivity at high temperatures is measurable at low temperatures. The vacancy equilibration is thus observable even at medium temperatures where the extra resistivity is small but the relaxation time is sufficiently long.

(c) The sample is subjected to such rapid oscillations in temperature that equilibration cannot follow them. This technique was used in measurements of the specific heat of supercooled liquids on approaching the glass transition [16–18] and in observations of the vacancy equilibration [19–23]. Under rapid temperature oscillations, the influence of the vacancies is almost completely excluded. This relates to properties that depend on changes of the vacancy concentrations during the measurements: specific heat, thermal expansivity, and temperature derivative of resistivity. If the vacancy concentration does not follow the temperature oscillations and retains a mean value, then these properties practically correspond to an ideal defect-free crystal. This method permits a reliable separation of vacancy contributions to the physical properties. A drawback of this approach arises from short equilibration times due to the high mobility of the vacancies at high temperatures and numerous internal sources (sinks) for them. Relaxation is therefore observable only at high frequencies of the temperature oscillations. The amplitude of the temperature oscillations is inversely proportional to their frequency, and the measurements require employment of special techniques.

2. ORDERING IN ALLOYS

Measurements of electrical resistivity are well-known as an effective tool for investigations of ordering in alloys. For example, the kinetics of the order–disorder transition in Cu_3Au alloy was studied through the electrical resistivity [7]. The relaxation time from the disordered state to the equilibrium state below the transition point is so long that the measurements can be carried out very easily. The sample was heated in a furnace at 673 K and then quenched to and kept at a certain temperature below the order–disorder transition, 664.2 K. The relaxation time increases rapidly when the temperature approaches the transition point (Fig. 1).

The kinetics of long-range ordering in a Ni_3Al compound was studied through measurements of resistivity [8]. The sample annealed at 1173 K was rapidly cooled to lower temperatures. An exponential decrease in resistivity at 862 and 880 K and increase at 925 and 973 K were observed. The inverted resistivity relaxation is in agreement with a phenomenological model [24, 25]. The observed changes in the resistivity never exceeded

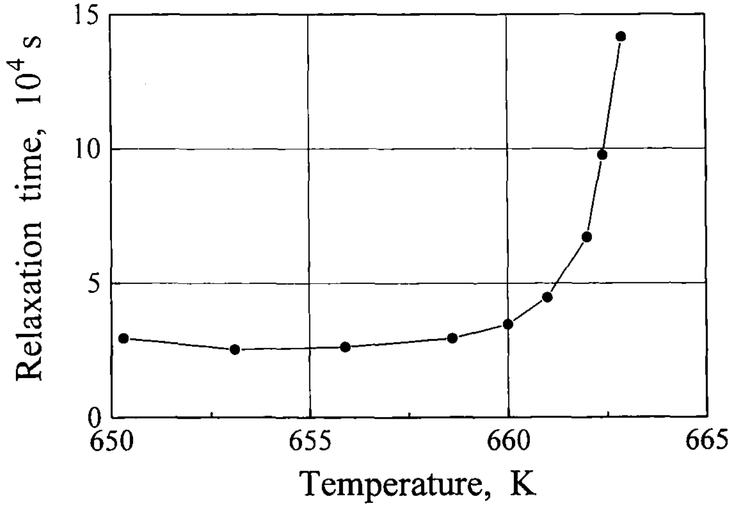

Fig. 1. Relaxation time in Cu_3Au alloy near the order–disorder transition point [7].

0.2% and the uncertainty in the relaxation times was estimated as 30%. The relaxation time in the range 862 to 973 K decreases from about 10^6 to 2×10^5 s.

A similar study of the short-range ordering in Au–Ag alloys has been reported [9]. When a constant value of resistivity was achieved, a small change in temperature, typically 10 K, led to another equilibrium value for the resistivity. The changes of the resistivity were of the order of 0.1%. In the range 450 to 520 K, the relaxation time decreases from about 10^5 to 10^2 s, also being dependent on the Ag contents. The activation enthalpy has been determined from the Arrhenius plot of the relaxation time. In contrast to the previous results, the relaxation did not obey exactly a pure exponential law.

An investigation of resistivity, along with measurements of the velocity of sound, has been performed in amorphous alloys FeCrB, FeMnB, and FeNiB [10]. In metallic glasses, structural relaxation occurs at temperatures sufficiently high to allow appreciable atomic motion but low enough to avoid crystallization. A slow relaxation of the resistivity of both signs was observed, being dependent on the composition and temperature.

In all the above examples, the relaxation times were very long. However, they rapidly decrease with increasing temperature. Subsecond thermophysical measurements may therefore become useful for studying ordering and structural relaxation at high temperatures.

3. GLASS TRANSITION IN SUPERCOOLED LIQUIDS

When a liquid is supercooled sufficiently below its equilibrium freezing point, it inevitably undergoes a glass transition into a state with thermodynamic properties appropriate for a solid. The characteristic relaxation times of the liquid increase rapidly as the transition point is approached. The specific heat of a supercooled liquid is greater than that of the crystal. The temperature at which the specific heat changes abruptly depends on the cooling or heating rate, while the specific heat of the liquid measured with the modulation calorimetry becomes frequency dependent.

A technique developed for modulation measurements [16–18] employs a thin-film heater (about 100 nm) evaporated on a glass substrate. It is immersed in the liquid to be studied. The heater serves also as a thermometer. When a current of frequency ω passes through it, the AC component of the dissipated power has a frequency of 2ω. The temperature and the resistance of the heater oscillate at this frequency. The voltage across the heater is the product of the current passing through it and its resistance which has a small component at frequency 2ω. A small signal at frequency

3ω therefore appears, being proportional to the amplitude of the temperature oscillations in the heater and to the temperature derivative of its resistance. This method, known as the third-harmonic technique, has been developed by Corbino [26], the founder of modulation calorimetry. A bridge circuit is employed to reduce the large signal of the fundamental frequency, and the third harmonic is measured with a lock-in amplifier. Temperature oscillations in the heater depend on the product of C, the specific heat, and k, the thermal conductivity of the liquid surrounding the heater. The measurements covered a frequency range of five decades. When the period of the temperature oscillations becomes comparable with the relaxation time, the quantity Ck contains both real and imaginary parts. The frequency corresponding to the change of the real part and the peak of the imaginary part depends strongly on the temperature (Fig. 2). It has been shown that the frequency dependence pertains only to the specific heat. The relaxation time obtained in specific-heat measurements has the same temperature dependence as that from other techniques.

Relaxation phenomena can also be studied through observations of the phase shift between the temperature oscillations and the corresponding changes in the chosen property of the sample. A modulation calorimeter has been reported [27] for a wide frequency range, also employing the third-harmonic technique.

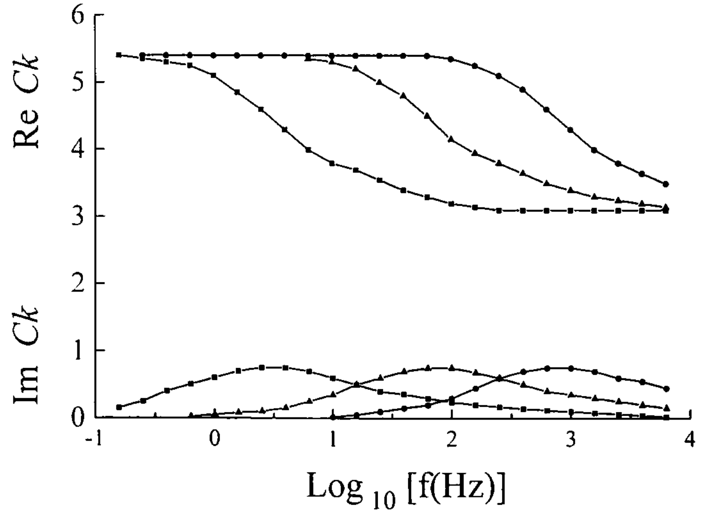

Fig. 2. Frequency dependence of the real and imaginary parts of the quantity Ck (in arbitrary units) in supercooled propylene glycol at three temperatures according to Ref. 17.

4. VACANCY EQUILIBRATION IN METALS

Observations of the vacancy equilibration are considered the most reliable method to separate vacancy contributions to physical properties of metals. The relaxation time, i.e., the characteristic time of setting up the equilibrium concentration, depends not only on the temperature and migration parameters but also on the density of internal sources (sinks) for the vacancies. The relaxation time, τ, is proportional to the square of the mean distance L between the sources (sinks) and inversely proportional to the coefficient of self-diffusion of the vacancies, D_V: $\tau = AL^2/D_V$, where A is a numerical coefficient depending on the geometry of the sources (sinks). Studies of the vacancy equilibration provide data for calculations of both formation and migration enthalpies of the vacancies.

The vacancy equilibration in gold, platinum, and aluminum was observed through the extra resistivity of the samples subjected to controllable exposures to high temperatures. In gold [13], two methods were used. First, thin single-crystal slabs were heated to 1150–1200 K with a rapid jet of hot compressed air, held for a short period of time, and then quenched. The frozen-in vacancies were detected by precipitating them as vacancy tetrahedra observable by a transmission electron microscope. Second, polycrystalline foils were pulse heated resistively to a high temperature, held at this temperature for durations ranging from 0.02 to 1.5 s, and then quenched. The extra resistivity after quenching was measured at 4.2 K. The half-times for the vacancy equilibration at 926 and 1151 K have been determined as 80 and 9.5 ms, respectively. The results indicated that free dislocations were the predominant vacancy sources in the samples. In studies on platinum [14], a wire sample was heated to a quench temperature by the discharge current of a capacitor at a rate of about $10^6\ \mathrm{K \cdot s^{-1}}$. Cool helium gas blown across the wire provided a rapid quench after termination of the heating current. For measuring the extra resistivity, the sample was immersed in liquid nitrogen or helium. The same technique was employed in studies on aluminum [15]. The extra resistivity due to vacancies in terms of the pulse-heating time was measured at temperatures from 583 to 673 K. The vacancy contribution to the resistivity and the migration enthalpy were calculated.

In another study [28], the vacancy equilibration in tungsten was monitored by interrupting quenches from 2900 K at well-defined temperatures from 1550 to 2600 K, followed by a quench to 300 K. The quenched-in resistivity was measured at 4 K. From the data obtained, migration enthalpy was found to increase from 1.68 eV at 1550 K to 2.02 eV at 2600 K. A similar temperature dependence of the formation enthalpy could explain the observed curvature in the Arrhenius plot of self-diffusion in tungsten.

The heat absorbed by the vacancy formation in aluminum was measured directly with a precision microcalorimeter [11]. The temperature of the calorimetry chamber was stabilized and the sample, held at a different temperature, was lowered into the thermopile. In the absence of thermal reactions in the sample, the output voltage of the thermopile varies exponentially. This was checked with a copper sample in which the vacancy contributions at these temperatures are negligible. If extra heat is absorbed or released by the sample, the output voltage no longer behaves exponentially. The extra heat was attributed to changes in the vacancy concentrations in the sample. The investigators believed that their results were underestimated because the initial part of the calorimetric curves could not be followed.

The vacancy contribution to the specific heat of refractory metals can be seen from the results of rapid-heating measurements. Specific heat values under rapid-heating conditions lie below equilibrium data at intermediate temperatures but increase rapidly when temperature approaches the melting point [2]. Such a behavior should be expected when the heating rate is high enough to avoid vacancy formation at intermediate temperatures but becomes insufficient at higher temperatures. If this interpretation is correct, then the total vacancy contribution to the enthalpy in such experiments should be the same as in equilibrium measurements.

The modulation calorimetry seems to be the most suitable technique to search for relaxation phenomena in specific heat. Attempts to observe relaxation with modulation frequencies up to 10^3 Hz were undertaken on gold and platinum. A gold wire was heated by an AC current, and the temperature oscillations were detected with the third-harmonic technique [19]. In this case, the measured quantity is C/R', the ratio of the specific heat of the sample to the temperature derivative of its resistance. This ratio increased along with the frequency of the temperature oscillations. This is quite understandable if the relative vacancy contribution to the specific heat is smaller than that to the temperature derivative of the resistance. Measurements have been performed at a single temperature, 1164 K, at frequencies up to 10^3 Hz. In platinum, the temperature oscillations were detected by the radiation from the sample, and no frequency dependence has been found [20]. Later, a method was developed for measurements at modulation frequencies of the order of 10^5 Hz. Using this approach, the expected relaxation phenomenon in the specific heat was observed in tungsten [21] and platinum [22]. The technique and results obtained have been recently reviewed [23].

Pulse-heating studies by positron annihilation spectroscopy were performed on gold [12]. The ^{22}NaCl source (5.5×10^5 Bq) was deposited in the central portion (8 mm) of a thin-walled tube of high-purity gold (diameter, 1 mm; length, 90 mm; wall thickness, 0.15 mm). The sample was heated in a helium atmosphere to an initial temperature by resistive heating. A superimposed capacitor discharge raised the temperature of the sample rapidly (0.5 ms) to a higher temperature kept constant during the measurement period. Then the sample was cooled to the initial temperature and the cycle repeated. The measurement period was divided into seven time intervals (Fig. 3). For each interval, the data on the positron lifetime and Doppler-broadening annihilation parameter were accumulated during about 10^6 pulses. Temperature of the sample was rapidly changed from 500 to 600 K, from 680 to 800 K, and from 790 to 900 K. No changes in the annihilation parameters were seen in the first case because of negligible vacancy concentrations. At 800 and 900 K, the relaxation times have been determined as 11.7 and 3.6 ms, respectively. Density of dislocations acting as vacancy sources has been estimated as $4 \times 10^8\,\mathrm{cm}^{-2}$. This high value is due to the mechanical stresses in the sample caused by the heating pulses.

The relaxation time in various samples may be very different. It also depends on the thermal history of the sample. As is known from quenching experiments, the difference may amount to several orders of magnitude. It is therefore useful to observe simultaneously the relaxation in various physical properties. Pure and well-prepared samples are necessary for the observations at higher temperatures.

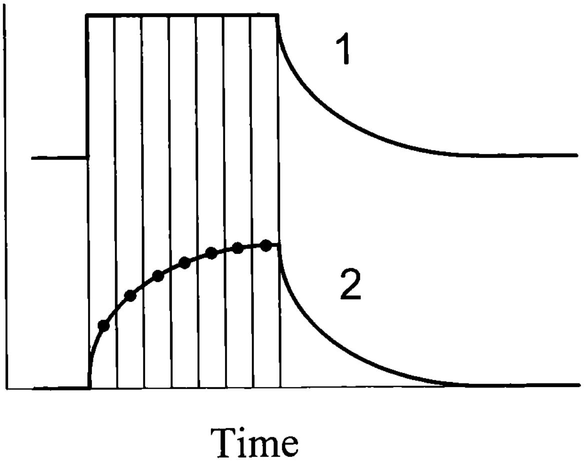

Fig. 3. Observation of vacancy equilibration with positron–annihilation spectroscopy [12]. (1) Temperature of the sample; (2) positron trapping rate.

5. PROPOSAL FOR SUBSECOND THERMOPHYSICS

Rapid-heating experiments may reveal the vacancy contributions to the enthalpy of metals. Under very rapid heating, the vacancies have no time to appear, so that the enthalpy at a given premelting temperature should be smaller than in equilibrium measurements. For molybdenum, the expected difference based on the supposed vacancy origin of the nonlinear increase in the specific heat amounts to about 10%. To check this assumption, an examination of typical data on molybdenum has been undertaken. They include equilibrium measurements of the enthalpy [29], millisecond-resolution measurements of the specific heat [30–33], and rapid-heating determinations of the enthalpy at the melting point [34–37]. Taking into account an estimated time of vacancy equilibration, only experiments with heating rates of the order of $10^8\ \mathrm{K \cdot s^{-1}}$ or more may be assumed not to include the vacancy contribution. Rapid-heating experiments usually start at room temperatures. To fit the specific-heat data obtained at high temperatures, the enthalpy at 1500 K was taken as $33.5\ \mathrm{kJ \cdot mol^{-1}}$ [29]. Certainly different values of the enthalpy at the melting point under equilibrium and rapid-heating conditions appear in the literature. To make a quantitative comparison, parts of the enthalpy related to the nonlinear increase in specific heat were separated from the results of equilibrium measurements. For this purpose, the experimental data were fitted by equations taking into account the vacancy contributions.

Thus we have three sets of data: (i) equilibrium enthalpies at the melting points after subtracting the supposed vacancy contributions, H_1;

Table I. Enthalpy of Solid Molybdenum at Its Melting Point[a]

H $(\mathrm{kJ \cdot mol^{-1}})$			
H_1	H_2	H_3	Investigators
83	89		Chekhovskoi and Petrov [29]
81	91		Rasor and McClelland [30]
84	92		Kraftmakher [31]
85	89		Cezairliyan [32]
83	90		Righini and Rosso [33]
		87	Shaner et al. [34]
		85	Seydel and Fisher [35]
		87	Hixson and Winkler [36]
		87	Pottlacher et al. [37]

[a] H_1, enthalpy after subtracting the assumed defect contribution; H_2, total enthalpy; H_3, results of rapid-heating experiments.

(ii) total equilibrium enthalpies, H_2; (iii) enthalpies from rapid-heating measurements, H_3, which are expected to be close to H_1 rather than to H_2. All the data are given in Table I. With heating rates of 10^8 to $10^9\ \mathrm{K \cdot s^{-1}}$, an uncertainty of 3–5% has to be assumed for the enthalpy [37]. The difference between H_1 and H_2 is therefore quite detectable. At present, the rapid-heating data, H_3, lie between the two values. The reasons may be as follows: (i) the heating is not fast enough to avoid vacancy formation completely, (ii) the superheat of the samples under rapid heating leads to higher enthalpies at the apparent melting point, and (iii) vacancy formation accounts for only a part of the nonlinear increase in specific heat. To check these possibilities, it is enough to vary the heating rates and determine the apparent melting point or to measure the enthalpy at a selected premelting temperature.

To determine vacancy contributions to enthalpy of metals at high temperatures, a more convenient and straightforward approach can be proposed. After heating the sample to a premelting temperature, the initial cooling curve depends on whether the vacancies had time to arise. If they did not, they will appear immediately after heating. At premelting temperatures, equilibrium vacancy concentrations set up in 10^{-4} to 10^{-2} s in low-melting point metals and in 10^{-8} to 10^{-6} s in refractory metals [23]. Under usual conditions, the temperature of the sample after heating, in the time region of interest, remains nearly constant. Therefore, heat absorbed by the vacancy formation after heating should be easily detected. The shape of the cooling curve depends on the vacancy contribution to the enthalpy and on the relaxation time, which depends strongly on the temperature.

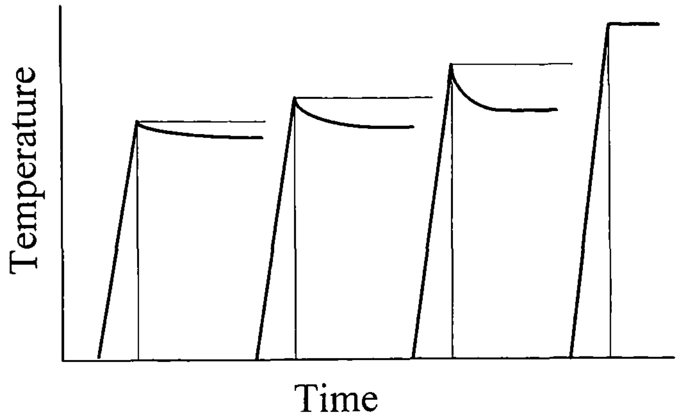

Fig. 4. Expected temperature records under rapid heating of metals. At the highest temperature, the vacancies have appeared during heating.

Heat absorbed by the vacancy formation will be seen from the decrease in the temperature of the sample immediately after heating. For molybdenum, the expected decrease is of about 200 K. If heating is not sufficiently fast, the phenomenon could be studied under gradually increasing the upper temperature of the sample. The decrease in the temperature immediately after heating must first increase with the temperature, reach a maximum, and then fall due to the decrease in relaxation time (Fig. 4). Also, it is easy to show that the decrease in the temperature of the sample after rapid heating should be accompanied by an increase in its volume. Such unusual behavior would be the best confirmation of the vacancy origin of the phenomenon. The proposed approach seems to be the simplest experiment that could be performed for the determination of equilibrium vacancy concentrations in metals.

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