Journal of Low Temperature Physics, Vol. 15, Nos. 3/4, 1974

On Mössbauer Thermometry in the Millikelvin Region

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(Received November 14, 1973)

Resonant absorption of γ-rays by ^{57}Fe and ^{119}Sn in iron was investigated to study the possibility of ultralow-temperature measurements by the Mössbauer effect. A dilution refrigerator which could provide temperatures down to 6 mK was used. The Mössbauer temperature of ^{119}Sn coincided with the temperature in the mixing chamber down to 6 mK if the heat input to the absorber was low enough ($\lesssim 10^{-5}$ erg/sec). But the Mössbauer temperatures of ^{57}Fe stayed almost invariable below 15 mK. In the same iron sample the nuclei of ^{57}Fe and ^{119}Sn had different Mössbauer temperatures below 15 mK. The reasons for this phenomenon are not yet clear.

1. INTRODUCTION

The possibility of application of the Mössbauer effect for absolute temperature measurements in the millikelvin region has been discussed repeatedly$^{1-3}$ but as far as we know it remains unrealized. In the present work an attempt is made to verify this possibility.

The theoretical foundations of the method are rather simple and are based on the following statements: First, the Zeeman sublevel populations (with the energy E_i) of nuclei are determined in thermal equilibrium by the Boltzmann factor $\exp(-E_i/k_B T)$, where k_B is Boltzmann's constant; second, the γ-ray emission or absorption probability is proportional to the initial state population. Therefore relative intensity measurements of appropriate Mössbauer spectrum lines allow to determine directly the absolute temperature of the nuclear spin system.

In practical realization of the Mössbauer thermometer two different methods are available, depending on whether the source or the absorber is the thermometer. The absorber method is preferable for the following reasons: First, the application of this method in real experimental conditions results in considerably smaller heat input to the absorber. Second, this method allows relatively simple control of the thermometer heating due to absorption of γ-rays by variation of their intensity. Third, a thermometer of this type is absolute in the sense that the required parameters for thermodynamic temperature calculations are determined directly from the absorption spectrum.

The problems of attainment of thermal equilibrium in investigated objects at ultralow temperatures are of great importance. Keeping these in mind, we have performed the measurements in such a way that we could carefully compare the Mössbauer thermometer with some other thermometer and control all the factors important in attaining thermal equilibrium.

As a reference thermometer cerium magnesium nitrite (CMN) was used, which has well-known thermometric properties. In our experiments resonance absorption of γ-rays by ^{57}Fe and ^{119}Sn nuclei in a ferromagnetic matrix was investigated. These two isotopes (especially ^{57}Fe) seem to be suited for Mössbauer temperature measurements in the millidegree region. Figures 1 and 2 show the Mössbauer spectra of one of our absorbers containing ^{57}Fe and ^{119}Sn nuclei. The diagram of transitions in the absorber, shown in Fig. 1, refers to ^{57}Fe nuclei; in the case of ^{119}Sn nuclei all the signs of the nuclear spin projections m should be changed to their opposites. In our case the interpretation of the experimental results is simple. The intensity ratio of symmetric absorption lines (corresponding to $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$ transitions, for instance) is (in a thin absorber)

$$p = (N_\infty - N_+)/(N_\infty - N_-) = \exp(\Delta/k_B T) \qquad (1)$$

where $N_\pm$ are the intensities of the γ-radiation at resonance (plus sign corresponds to source movement toward the absorber), and N_∞ is the intensity far from resonance.

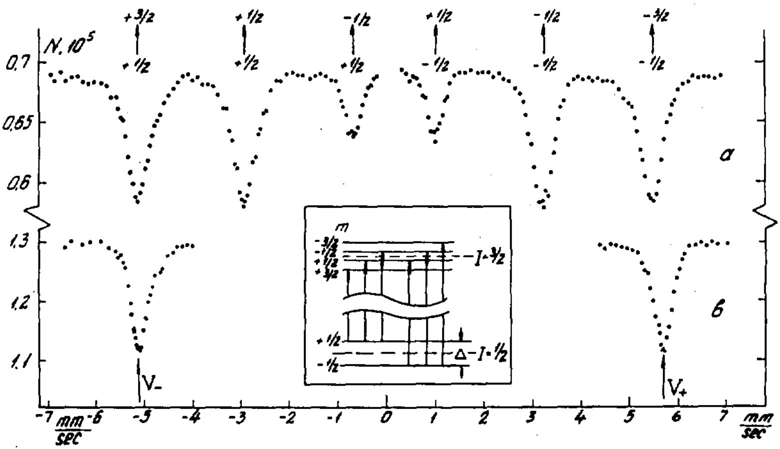

Fig. 1. The Mössbauer spectrum of ^{57}Fe nuclei for absorber 5. (a) $T = 300$ K (b) $T = 1.2$ K (outer lines of the spectrum only). The source is ^{57}Co in Cr.

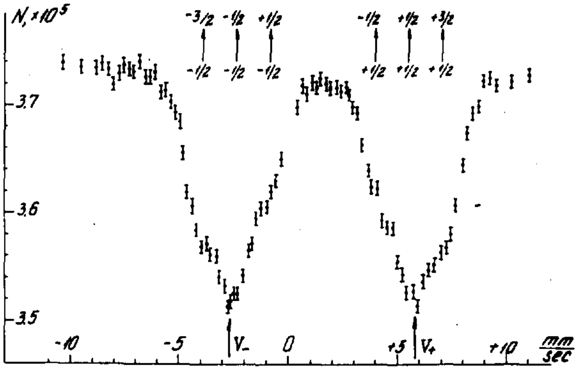

Fig. 2. The Mössbauer spectrum of ^{119}Sn nuclei in absorber 5 at $T = 1.2$ K. The source is ^{119m}Sn in SnO_2.

2. THE CRYOSTAT

To cool the absorbers, a simple dilution refrigerator was used, similar to that described in Ref. 4. Figure 3 shows a general view of the device. The refrigerator provided temperatures to 30 mK in continuous mode and to 5–6 mK when single cycling. The construction of the tube-in-tube heat exchanger (total length about 1.5 m) was selected to provide stable functioning of the device at a rather low circulation speed ($\sim 10^{-5}$ mole/sec). To achieve this, the distance between the external and the internal tubes in the upper part of the exchanger where conditions for convection are favorable was decreased to 0.2 mm. The external capillary diameter (German silver, wall thickness 0.2 mm) was gradually increased from top to bottom to 2.5 mm at the mixing chamber entrance. This construction is necessary to minimize the heat input to the chamber in a single-cycle regime, when the viscous heating inside the tube becomes serious. Moreover, the return line volume, with warmer ^{3}He, was of minimum possible value (about 0.05 cm^3) to make the performance of the single cycle more efficient. To decrease the heat input to the mixing chamber from the vacuum jacket walls and increase the mechanical rigidity of the colder stage, a steel screen was tightened to the middle part of the heat exchanger. The screen and the chamber were centered by a system of Teflon rings. All these measures provided a decrease of the total heat input to the mixing chamber in single cycle to an acceptable value (of the order of 0.1 erg/sec). For general control of the refrigeration process a speer carbon resistance thermometer was used.

All the walls of the lower part of the cryostat were made of 0.5-mm-thick beryllium (total thickness of beryllium 5 mm). Such a construction was much more compact than designs utilizing beryllium windows, though

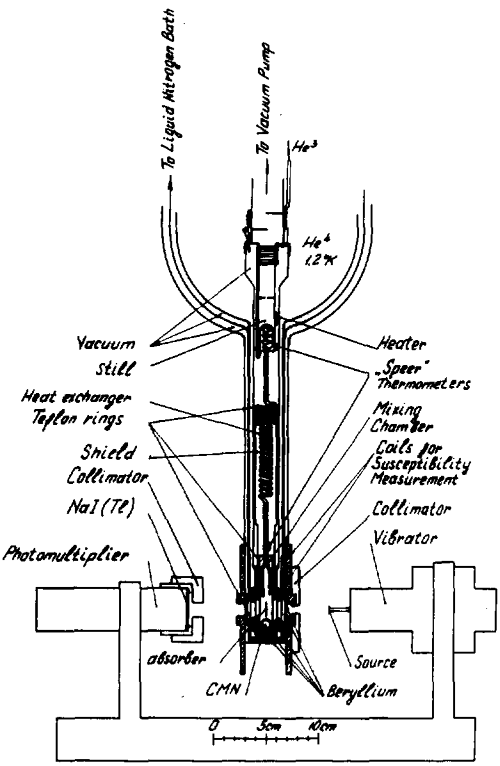

Fig. 3. The general view of the cryostat.

we had some technological difficulties in making the system vacuum-tight. The beryllium "pistons" were glued* to copper or steel pipes by Epibond 100A. To decrease γ-ray absorption, beryllium of 99.95 % purity was used. Nevertheless, a small (2–3 %) resonant γ-ray absorption was observed due to the presence of iron residues in beryllium for the ^{57}Co source at low source velocities (0 ± 0.5 mm/sec).

The mixing chamber (Fig. 4) was a 74-mm-long cylinder with external diameter 13 mm. The chamber was covered by a copper cap and soldered with a soft solder. To tighten the absorber and thermally isolate it from the walls,† a thin (0.5 mm) Textolite frame was used. The temperature in the

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*Beryllium can be soldered to copper in vacuum with silver solder. However, it is difficult to achieve vacuum-tight soldering. Moreover, such solder becomes superconducting at temperatures of about 0.4 K and interferes with CMN susceptibility measurements. The soldering of precoppered beryllium with soft solder was rejected for the same reason.

†According to our estimates, the temperature of the chamber walls can exceed the temperature of the liquid inside the chamber by 10–15 mK.

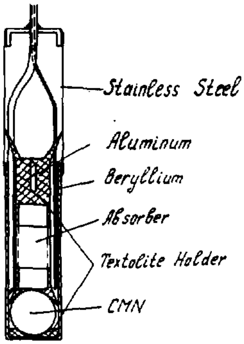

Fig. 4. The mixing chamber.

mixing chamber was measured by means of the magnetic susceptibility of a spherical sample (powder of 1.90 g/cm^3 density) of CMN.

The susceptibility was measured by a ballistic method (the measuring field was 1–2 Oe). The sensitivity of the system was calibrated in a special experiment by the magnitude of the magnetic moment change of a tin ball at its superconducting transition. Moreover, in two special experiments demagnetizations of the salt were performed from temperatures of about 10 mK and a magnetic field of 300 Oe. The deflection of the ballistic galvanometer after demagnetization was the same in both cases. It stayed constant with accuracy better than 1% for 5 and 30 min. This maximum deflection corresponded to 2.3 mK (if the Curie constant $C = 2.77 \times 10^{-4}$ K/g is used for the powder sample). As a reference point the temperature of the superconducting transition (1.1 K) of the aluminum sample was used. Supposing that the susceptibility of CMN above 6 mK obeys Curie's law and taking into account all the possible systematic errors, the accuracy of the measurements can be estimated as 5% in the temperature range from 6 to 100 mK. The thermal relaxation time between CMN and the liquid in the mixing chamber was measured in special experiments in which demagnetizations of the CMN under various temperatures from low magnetic field (30–60 Oe) were performed. The maximum registered relaxation time was 5 min (at a temperature of about 5 mK).

The apparatus enables us to maintain constant temperature with accuracy not worse than 5% during not less than 1.5 h in the range of 7–20 mK, and not less than 4 h in the range of 20–100 mK. The temperature adjustment was performed by variation of the heater power at the still. The time of cooling from 1 K to 34 mK was about 2 h and from 30 to 6.0 mK was about 3 h.

3. THE MEASUREMENT PROCESS AND THE SAMPLES

In our experiments a constant-velocity Mössbauer spectrometer was used with independent stabilization of positive and negative velocities.[5]

The spectrometer provided easy adjustment to any velocity in the range of 0.5–10 mm/sec with accuracy and long-term stability better than 0.001 mm/sec; the velocity resolution of the spectrometer was better than 0.01 mm/sec and was determined by velocity fluctuations during the counting time (0.16 sec) of each half-period.

The γ-ray sources and the scintillation detector were located outside on a massive frame. At a sample temperature of about 1.2 K the spectrometer was tuned to a pair of symmetric absorption lines and carefully adjusted to eliminate the possible geometric difference of counting rates N_+ and N_-. In this process the line intensities in general appeared to be different; however, the difference did not exceed several percent of each line intensity; for temperature determination a corresponding correction was introduced. The counting rate N_∞ remained constant with accuracy 0.5% during each experiment and was periodically controlled. The magnitude of p [see Eq. (1)] could be measured during all the cooling and reverse heating processes (the counting time was 20 min; the typical number of impulses at each counting channel was 10^6). When the finite time resolution of the spectrometer is taken into account (the dead time of the discriminator was $\tau = 1 \times 10^{-5}$ sec), one gets the following expression for corrections to the measured magnitude:

$$(\ln p)_\tau = (\ln p)_{\tau \to 0} + (N_- - N_+)(\tau/t)$$

where t is the total measurement time in each channel (usually $t = 335$ sec). If $T > \Delta$, then $N_- - N_+ \sim \Delta/T$ and the effect reduces to an insignificant (less than 1%) renormalization of the magnitude of Δ. We used the following samples as cooled absorbers (see Table I). Absorbers 1 and 2 were rolled foils of Carbonil natural (2.19% ^{57}Fe) iron (0.1% impurities) containing 0.12 and 2×0.12 mg/cm^2 of ^{57}Fe, respectively. Absorbers 3 and 4 were iron foils with 89% ^{57}Fe containing 0.31 and 2×0.17 mg/cm^2 of ^{57}Fe, respectively. These foils were made by electrolysis in a $FeSO_4$ solution on a copper foil, which was then dissolved.[6] Then the enriched foils were glued

TABLE I

The Characteristics of the Absorbers Investigated

No.	d_{tot}, mg/cm^2	$d(^{57}$Fe), mg/cm^2	$d(^{119}$Sn), mg/cm^2	$\bar{\Delta}$, mK	a	b	ρ_0, $\mu\Omega$-cm
1	5.4	0.12	—	2.23 ± 0.02	0.88 ± 0.01	0.01	1.6
2	10.8	0.24	—	2.23 ± 0.02	0.77 ± 0.02	0.02	1.6
3	0.35	0.31	—	2.23 ± 0.02	0.76 ± 0.02	0.02	2.5
4	0.38	0.34	—	2.23 ± 0.02	0.75 ± 0.02	0.02	2.5
5 ^{57}Fe	22.3	0.48	—	2.22 ± 0.03	0.71 ± 0.02	0.02	6.7
^{119}Sn		—	0.68	5.8 ± 0.3	0.81 ± 0.03	0.015	
6	9.2	0.32	—	2.03 ± 0.05	0.88 ± 0.02	0.01	75

onto a 0.2-mm-thick beryllium strip. Absorber 5 was an iron foil containing 1.5 at % of ^{119}Sn prepared in the following way: The ^{119}Sn isotope was evaporated in vacuum and condensed on the iron foil surface (No. 1), which was then heated in hydrogen for 3 h. The total thickness of the sample was 0.48 mg/cm^2 of ^{57}Fe and 0.68 mg/cm^2 of ^{119}Sn. Absorber 6 was a rolled foil of Permalloy (75 % Ni, 25 % Fe) obtained by fusion of high-purity Ni and Fe, enriched by the ^{57}Fe isotope to 14 %. The sample thickness was 0.32 mg/cm^2 of ^{57}Fe.

The magnitudes of Δ at helium temperature and the electrical resistivities at helium temperature ρ_0 are given in Table I. Standard Mössbauer sources of ^{57}Co in Cr and Pt and ^{119m}Sn in SnO$_2$ were used for the measurements. The activity of the ^{57}Co varied from 1 to 10 mCi, and of ^{119m}Sn was about 10 mCi. The absorption linewidth measured with the ^{57}Co source was determined mainly by the level of the absorber vibrations during the experiment and for typical conditions was 0.5–0.6 mm/sec (Fig. 1), except for sample 6, for which the outer linewidth in the absorption spectrum was 0.8 mm even in the absence of vibrations. The absorption spectrum for sample 5 measured with the ^{119m}Sn source was an overlapping of six lines, each about 2 mm/sec width (Fig. 2). When calculating the Mössbauer temperature T_M from the measured magnitude of p one should take into account the fact that Eq. (1) is valid only for infinitely thin absorber. The corrections for finite thickness of the absorber can be calculated if the linewidths and effective thicknesses of the source and the absorber are known.[7]

When $T_M > \Delta$ the desired relation can be conveniently represented as a series.

$$\ln p = a(\Delta/T_M) + b(\Delta/T_M)^3 + \cdots \qquad (2)$$

where the coefficients $a, b, \ldots$ are resonant parameters, functions of the source and the absorber. The numerical magnitudes for the coefficients a and b for $\pm\frac{1}{2} \rightarrow \pm\frac{3}{2}$ transitions are given in Table I. Note that the second term is small compared with the first one.

It is necessary to use a relation more precise than (1) in the case when the magnitude Δ is not strictly constant (due to variation of magnetic field at different nuclei, for instance). In this case instead of (1) we have

$$\ln p = \frac{\bar{\Delta}}{T_M} - \frac{\overline{(\Delta - \bar{\Delta})^2}}{2T_M^2} \tanh \frac{\bar{\Delta}}{2T_M} \qquad (3)$$

where $\bar{\Delta}$ is the mean value of Δ, with mean square deviation $[\overline{(\Delta - \bar{\Delta})^2}]^{1/2}$ (dispersion), which is supposed to be small compared to T_M. For our absorbers the second term in (3) is negligible (< 1 % of the first). When the dispersion Δ is taken into account there also arise temperature-dependent line shifts; however, in our experiments these shifts were too small to be detected.

4. EXPERIMENTAL RESULTS

The experiments with the samples 1–4[8] gave the following results [see Fig. 5 for samples 2 and 3, where the Mössbauer temperature T_M was calculated from Eq. (2)]. In all cases the measured magnitude of ln p tended to saturate below 15 mK; the deviations from the expected dependence $T_M = T$ exceeded considerably the experimental errors. There was no dependence of the measured magnitude on the rate of change of temperature. Therefore it can be concluded that the relaxation time between the nuclear spins and the liquid helium surrounding the sample was less than the time of measurement. A trivial reason for the observed $T_M(T)$ dependence could be heating due to γ-ray absorption. However, in the samples 3 and 4 this heat input was at least one order of magnitude less than for samples 1 and 2. Moreover, control experiments showed that when the irradiation intensity of sample 4 was decreased ten times, T_M remained constant within an accuracy of 10% (at the same temperature). We have also performed control experiments to check on other possible sources of sample heating (external variable fields, mechanical vibrations, heat input from the chamber walls through the Textolite). In all cases at the same temperature, T_M remained the same within the limit of the statistical errors.

To check other possible reasons for the observed deviations, a more detailed investigation of the absorption spectrum at $T < 10$ mK was performed. Figure 6 shows the experimental results on the outer lines of the absorption spectrum for sample 3 at different temperatures. It can be seen that there are no noticeable shifts or broadenings of the lines down to the lowest temperatures investigated. Similar results were obtained for other pairs of spectral lines. The total area of the absorption spectrum remained constant within an accuracy of 5%.

The experiments with absorber 5, containing two kinds of resonant nuclei,[9] showed a distinct dependence of the measured results with ^{119}Sn nuclei on heat input to the sample (Fig. 7). The temperature T_M tended to T with decrease of heat input. Because of this result, we undertook a systematic investigation of the dependence of the results on heat input due to γ-ray

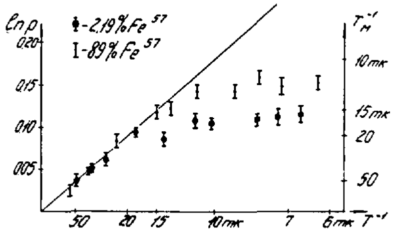

Fig. 5. The Mössbauer spectrum asymmetry vs. temperature for the absorbers 2 and 3.

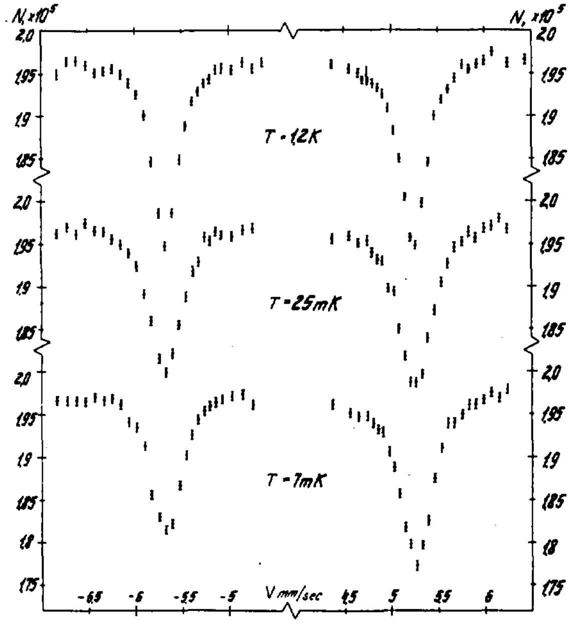

Fig. 6. The outer lines of the spectrum for the absorber 3 at different temperatures. The source is ^{57}Co in Pt.

absorption for all the samples (including no. 6). The heat input was calculated from the known source activity, the intensity distribution of its spectrum, and the geometry of the experiment. In these calculations tables of x-ray absorption were used.[10] When the ^{57}Co in Cr source is used the main absorption is due to the 14.4-keV line; in case of ^{57}Co in Pt source the

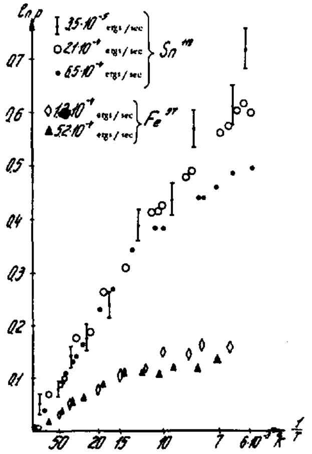

Fig. 7. The asymmetry of the Mössbauer spectra of ^{57}Fe and ^{119}Sn for the absorber 5.

x-ray radiation of Fe and Pt gives rise to comparable absorption. In experiments with enriched absorbers (nos. 3 and 4) the absorption in the Be backing is an order of magnitude higher than in the absorber itself. In special experiments performed with absorber 5 on ^{119}Sn nuclei with simultaneous irradiation by the ^{57}Co source it was found out that the character of the function $T_M(T)$ depends only on the total heat input to the absorber. The same result was obtained in experiments in which the ratio of the intensities of Mössbauer (23.8 keV) and x-ray (25.8 keV) lines in the ^{119m}Sn source was varied by Pd filters of different thicknesses. According to our estimates, the accuracy of the measurement of the heat input value is 20–30 %.

These measurements show that the observed deviations of T_M from T are considerably higher for ^{57}Fe nuclei than for ^{119}Sn in the same sample and for the same heat input (see Fig. 8, which shows the measured value of the Mössbauer temperatures for ^{57}Fe nuclei as a function of the Mössbauer temperatures for ^{119}Sn nuclei, with constant heat input). Therefore the observed deviations of T_M from T for ^{57}Fe and ^{119}Sn nuclei have to be of a different nature. Since in all cases the measured dependence of $T_M(T)$ tends to saturation when T is sufficiently small (the only exception is shown in Fig. 7), an attempt can be made to describe all the processes in a single way by calculating the limit of the Mössbauer temperature T_0 as a function of heat input when $T \to 0$, for all of our samples. Such an extrapolation can be based upon the relation

$$T_M^n - T^n = T_0^n \tag{4}$$

where n and T_0 should be selected each time to obtain the best correlation with the experimental dependence of $T_M(T)$. In most cases the magnitudes of T_0 calculated in such a way did not differ (within the limits of our accuracy) from the minimum measured values of T_M; they were not strongly sensitive to the selection of the n value (the best values for n lie between four and six).

Figure 9 shows the dependence of T_0 on heat input per unit area of the absorber surface W. The values for ^{119}Sn are in good agreement with the

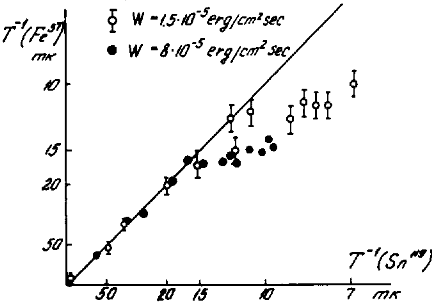

Fig. 8. Comparison of ^{57}Fe and ^{119}Sn Mössbauer temperatures at fixed heat input for absorber 5.

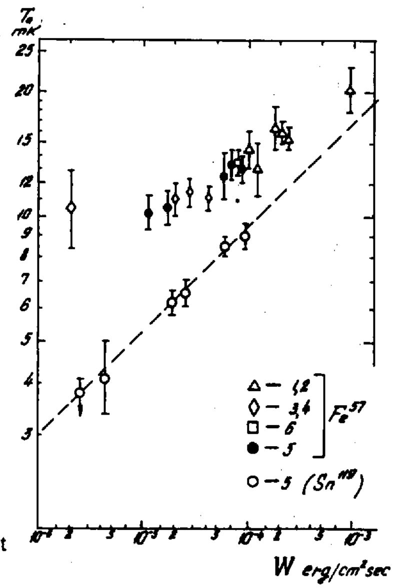

Fig. 9. The Mössbauer minimal temperature vs. heat input *W*.

dependence $T_0^4 \propto W$ (dashed straight line), which is to be expected in the case of sample overheating due to the Kapitza boundary resistance. In this case for the magnitude of the Kapitza boundary resistance we obtain

$$\delta T/W = (200/T^3) \quad \mathrm{K\,cm^2/W}$$

which corresponds to the measurements at higher temperatures.[11] The data for ^{57}Fe nuclei probably correspond for all the samples to some unique dependence $T_0(W)$ which is weaker than for ^{119}Sn nuclei (the values of *W* for samples 3 and 4 in Fig. 9 correspond to the total heat input to the samples and to the beryllium backing).

We cannot propose any sure explanation of all the results. Logically there exist two possibilities. The first possibility suggests some interaction between nuclear spins leading to nonzero population of the higher Zeeman sublevel of the ^{57}Fe ground state at 0 K. In this case the value of T_M should not tend to zero at $W \to 0$ (see Fig. 9). This proposal is very improbable because this kind of interaction should be extremely powerful (stronger than hyperfine); it does not depend on the nuclear spin concentration and in no way affects the hyperfine structure of the Mössbauer spectrum.

Therefore another explanation of the results is more likely. This is based on the proposal of an absence of thermal equilibrium in our absorbers. In this case it is essential that the direct heat input to the nuclear spins is very small; the energy absorbed by a single nuclear spin from γ-rays with

$E_\gamma = 14.4\,\mathrm{keV}$ or $23.8\,\mathrm{keV}$ must not exceed $\Delta \approx 10^{-11}E_\gamma$. As a matter of fact the absorbed energy is distributed among the conducting electrons, phonons, spin waves, and so on. A determination of the "temperatures" of each of these energy reservoirs is not at all a trivial problem. We do not have sufficient information about all the essential relaxation mechanisms (including nuclear relaxation mechanisms) to explain the observed anomaly. We can only state that the results obtained (especially the contradiction between the readings of the two nuclear thermometers in the same sample) show that it is necessary to be extremely careful when measuring the temperature by different thermometers in the millidegree region. This applies particularly to the method based on measurement of the anisotropy of oriented nuclei γ-radiation, because the difficulties connected with radioactive heating of the sample are more inherent in this method than in ours.

ACKNOWLEDGMENTS

The authors thank P. L. Kapitza for constant interest in this work, and B. G. Egiasarov, A. I. Shamov, and V. P. Romashko, who have provided the reliable work of the Mössbauer spectrometer, and D. V. Pavlov for his assistance in the experiments.

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