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MEASUREMENT OF THE NUCLEAR SPECIFIC HEATS OF IRIDIUM AND RHENIUM IN IRON ALLOYS

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A method is described for measuring very small nuclear specific heats and for estimating nuclear relaxation times in alloys. The nuclear specific heats of Re-Fe and Ir-Fe alloys of various concentrations are measured. The effective magnetic fields acting on the nuclei of the alloying metals are determined: $H_{eff} = (6.7 \pm 0.7) \times 10^5$ Oe for Re and $(1.35 \pm 0.3) \times 10^6$ Oe for Ir. The magnetic moment of Ir^{192} if found to be $(1.8^{+0.6}_{-0.5})\mu_n$.

IN 1958 Samoĭlov, Sklyarevskiĭ, and Stepanov discovered that an effective magnetic field H_{eff} of the order of 10^5—10^6 Oe acts on the nuclei of elements introduced into ferromagnets.[1] At sufficiently low temperatures the interaction of this magnetic field with the nuclear spins results in the polarization of nuclei and in the appearance of a nuclear component of the specific heat. Measurements of the nuclear specific heat and of the angular distributions of γ and β rays from polarized nuclei can often be used to determine H_{eff} and μ (the magnetic moment) of a radioactive isotope.

In addition to investigating the γ anisotropy and β asymmetry of oriented radioactive nuclei,[2] the nuclear specific heats of iron alloys with Ir and Re were measured in our laboratory. We describe here the experimental technique and present measurements of the specific heats.1)

1. TECHNIQUE OF MEASURING NUCLEAR SPECIFIC HEATS

The specific heat of an alloy is represented by $C_v = AT^3 + \gamma_{el}T + C_n$. When $kTI \gg \mu H_{eff}$ the nuclear specific heat of the alloy is given with sufficient accuracy by[3]

$$C_n = \gamma_n T^{-2}, \quad \gamma_n = \frac{1}{3} RI(I+1)(\mu H_{eff}/kI)^2,$$

where I is the nuclear spin of the particular element, μ is its magnetic moment, k is Boltzmann's constant, and R is the gas constant.

In order to determine H_{eff} in a minimally distorted lattice of a ferromagnetic solid solvent, alloys with low concentrations of the alloying element must be studied. When μH_{eff} is small in the alloy it is difficult to distinguish the nuclear specific heat of the alloy against the background of electronic specific heat even at $T \sim 0.1$°K. Therefore it is necessary:

1) To use a ferromagnetic solvent of low intrinsic nuclear specific heat. Pure iron, having a nuclear specific heat represented by $C_n T^2/R \leq 1.1 \times 10^{-8}(°K)^2$, satisfies this requirement.

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1) Reported at the 9th All-union Conference on Low-Temperature Physics (Leningrad, June, 1962) and also at the 8th International Conference on Low-temperature Physics (London, 1962).

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2) To obtain measurements at the lowest possible temperatures, so that the electronic component of the alloy's specific heat will be small (the electronic specific heat of an alloy obeys $C_{el} \sim T$, leading to the ratio $C_n/C_{el} \sim T^{-3}$). Our measurements were made in the range $0.05 \leq T \leq 0.2$°K.

The specific heats of the alloys were measured by comparing them with the specific heat of the cooling mixture (a 50% saturated aqueous solution of cerium-magnesium nitrate and 50% glycerin by volume). The adiabatic demagnetization of this mixture generates an extremely low temperature. The specific heat of the cooling mixture was determined in control experiments by comparison with the known [4] specific heats of metallic cobalt and of Fe-Co alloys with different concentrations.

It is known that thermal equilibrium between a system of nuclear spins and conduction electrons is established after some finite relaxation time. This fact served as the basis for the specific heat measurements.

In the system consisting of the cooling mixture (also serving as a thermometer) and a given sample, connected to the former by a "cold pipe," we produced pulsed disturbance of thermal equilibrium between the "electronic stage" (the specific heat of the cooling mixture and of conduction electrons in the cold pipe and sample) and the "nuclear stage" (the specific heat of the nuclear spin system in the sample). By investigating the establishment of equilibrium it is possible to determine the ratio between the nuclear specific heat of the sample and the specific heat of the cooling mixture.

Figure 1 represents the relation between the reciprocal temperature $1/T_c$ of the cooling mixture and the time required for one measuring cycle. Until the time t_1 the sample, cooling mixture, and cold pipe are slowly heated by parasitic heat flow; thermal equilibrium exists during this process. Pulsed heating of the electronic stage occurs during the time from t_1 to t_2; equilibrium is reestablished between the electronic and nuclear stages following a certain relaxation time.

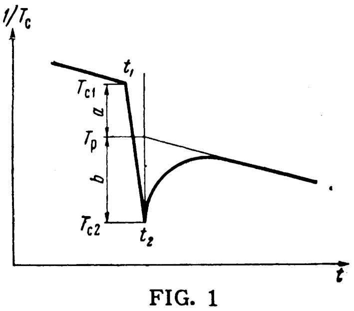

FIG. 1

Extrapolating the straight line representing the natural heating of the system following the establishment of equilibrium to the time t_2, we obtain the quantities a and b corresponding to the equilibrium temperature T_{equ}, and determine thereby the ratio of the nuclear specific heat of the sample to the specific heat of the cooling mixture. For this purpose it is necessary to take into account the electronic specific heat of the sample and cold pipe and the temperature change of the sample's nuclear stage during heat pulse. If the thermal resistances of the cooling mixture and of the contacts between the cooling mixture and cold pipe, and between the cold pipe and the sample, are small enough so that equilibrium is not destroyed in the electronic stage during a heat pulse, we can write the calorimetric equation

$$\int_{T_{c1}-1/\Delta}^{T_{equ}} \gamma_n T^{-2} dT + \int_{T_{c2}}^{T_{equ}} \gamma_c T^{-2} dT + \int_{T_{c2}}^{T_{equ}} \gamma_{el} T dT = 0. \qquad (1)$$

Here $C_c = \gamma_c T^{-2}$ is the specific heat of the cooling mixture, and γ_{el} characterizes the combined electronic specific heat of the cold pipe and sample. By integrating we obtain

$$\gamma_n/\gamma_c = [b + (\gamma_{el}/2\gamma_c)(T_{c2}^2 - T_{equ}^2)]/(a - \Delta), \qquad (2)$$

where $\Delta = 1/T_{n1} - 1/T_{n2}$ is the change in the reciprocal temperature of the nuclear stage during the heat pulse.

In order to determine Δ we use an equation describing the time variation of the energy level population in the nuclear spin system:

$$-dn/dt = (n - n_0)/\tau, \qquad (3)$$

where τ is the relaxation time characterizing the rate of equilibrium establishment between the nuclear spins and the lattice (in metals, as we know,[5] $\tau = \tau_0/T_{el}$, where τ_0 is a constant); T_{el} is the temperature of the electronic stage, and in our case is the temperature T_c of the salt; n_0 is the difference between the populations of two neighboring nuclear levels for $T = T_n = T_c$; and n is the difference between the populations of two neighboring nuclear levels for $T = T_n \neq T_c$.

The principal interaction determining the nuclear orientation in ferromagnets is magnetic; therefore the nuclear levels are spaced uniformly and τ will be identical for all levels of the spin system.[5]

When $kT \gg \Delta E = \mu H_{eff}/I$ and the temperature change during a heating pulse satisfies $\Delta T \ll T$ the nuclear level population at any time is represented by a Boltzmann distribution. Thus

$$n_0 = n_{0m} - n_{0m+1} = ce^{-m\beta_c}(1 - e^{-\beta_c}) \cong c\beta_c,$$
$$n = n_m - n_{m+1} \cong c\beta_n, \quad \beta = \mu H_{\mathrm{eff}}/kIT,$$

where m is the projection of the nuclear spin on the direction of nuclear alignment.

Equation (3) now becomes

$$dT_n/dt = (T_n/\tau)(1 - T_n/T_c). \tag{3a}$$

Here T_n and T_c are the temperatures of the nuclear and electronic stages. This equation is solved assuming $1/T_c = 1/T_{c1} - \alpha t$, where α is a constant; this condition is practically always satisfied in our experimental work. In this case we obtain

$$\Delta = \frac{(a+b)T_{c1} - \alpha\tau_0\{1 - [1 - (a+b)T_{c1}]^{1/\alpha\tau_0}\}}{T_{c1}(1 - \alpha\tau_0)}. \tag{4}$$

If $(a + b)T_{c1} \ll 1$ and $(t_2 - t_1)T_{c1}/\tau_0 \ll 1$, we have with sufficient accuracy

$$\Delta = (a+b)(t_2 - t_1)T_{c1}/2\tau_0. \tag{4a}$$

It is possible to calculate τ_0 from (2) and (4a) by measurements obtained at definite temperatures but with different heating periods. Assuming that in any one experiment γ_n/γ_c is a constant, measurements with two different heating periods yield a difference between the values of Δ for these two cases; using (4) or (4a) we then calculate τ_0. We note that the experimentally determined value of τ_0 cannot be regarded as the nuclear relaxation time because the thermal resistances of the cold pipe and of its contact with the sample are not zero. This circumstance has practically no effect on the specific heat measurements (see below), since the electronic specific heat of the sample makes only a small contribution to the total specific heat of the system. The experimentally determined value will therefore be denoted by τ_{0e}.

In writing the calorimetric equation it was assumed that the specific heat of the cooling mixture in the working temperature range obeys the law $C_c = \gamma_c T^{-2}$. Since this mixture also served as a thermometer, observance of the Curie law is also required. For crystalline cerium-magnesium nitrate both laws hold true at temperatures above 0.01°K. Detailed measurements were not obtained for the cooling mixture, but its specific heat measured in the present work practically coincides with the specific heat of the nitrate crystal. Any additional interactions in the cooling mixture are relatively weak. We therefore have no reason to expect any appreciable departures from the Curie law or from the law $C_c = \gamma_c T^{-2}$ in the working temperature region ($T \geq 0.05$°K).

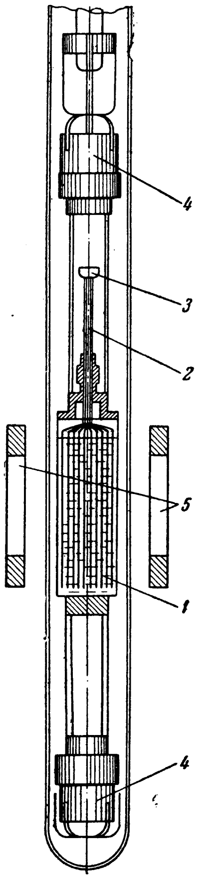

FIG. 2

2. DESCRIPTION OF APPARATUS

Figure 2 shows the apparatus used to measure the specific heats. The container 1 holds the cooling mixture, which is in thermal contact with the copper-plate "cold pipe" 2 having 300-cm^2 contact area and 0.6-mm plate separation. The alloy sample 3 is soldered to the cold pipe. In order to improve the thermal contact between the cold pipe and the sample their ends are covered with an electrolytic silver layer. Two "guard" blocks of chromium potassium alum 4 are positioned above and below the container 1.

The temperature of the cooling mixture is determined from its magnetic susceptibility by means of a self-induction bridge with 430 cps working frequency. Bridge unbalance is registered by an ÉPP-09M automatic recorder (with 1 sec required for traversal of the scale by the carriage). The flat coils 5 serve for pulsed heating of the cooling mixture using a 2500-cps field; almost all the heat is transferred to the cold pipe.

Table I. Nuclear specific heats of ferromagnets and ferromagnetic alloys

No. of sample	Alloy	Content, at. %	Weight of sample, g	γ, erg-deg (specific heat of sample γT^{-2})	$(CT^2/R)\cdot 10^6$, $(°K)^2$ *		τ_{0e}, sec-deg
					Cooling mixture	Alloy	
1	Fe	Fe, 100	1.0	$\leqslant 0.3$		$\leqslant 0.2$	
2	Fe—Co	Co, 3	0,27	13.7	7.3 ± 0.8	1150 ± 105	0,4
3	Fe—Co	Co, 0.5	1.85	14,0	7.2 ± 0.7	1180 ± 106	0.4
4	Co	Co, 100	$1.5\cdot10^{-3}$	12,0	7.2 ± 0.7	550 ± 45	0.4
5	Fe—Ir	Ir, 9.0	1.06	4.8 ± 1.0		36 ± 8	0.75
6	Fe—Ir	Ir, 6.1	2.24	7 ± 1.5		37 ± 8	0,75
7	Fe—Re	Re, 0.15	1.5	10 ± 1.8		2800 ± 500	0.6

*Samples Nos. 2, 3, and 4 served to determine the specific heat of the cooling mixture. The values of CT^2/R and the specific heats of the samples were calculated from data in [4]. CT^2/R for the alloys was calculated per gram-atom of the alloying element. For all alloy samples a correction was made for the measured specific heat of iron.

3. DISCUSSION OF RESULTS

The specific heat measurements are given in Table I. The specific heat of the cooling mixture was determined by a comparison with the specific heats of two Fe-Co samples having different concentrations and of a sample of metallic cobalt. The results exhibit good mutual consistency. Figure 3 shows the experimental dependences of $1/T$ on time for pure iron, metallic cobalt and a Fe-Ir alloy.

The existing theory provides only a qualitative description of the mechanism whereby an internal magnetic field is generated. According to Freeman and Watson [6] the field is associated with the interactions between unpaired electrons of the ferromagnet and s electrons of the alloying ions. On this basis for nonmagnetic alloying element the dependence of H_{eff} on atomic number should be monotonic.

The magnitudes of H_{eff} for iridium and rhenium differ by a factor of almost two, i.e., by more than expected for elements having close atomic numbers. It is possible that the effective fields for these ions are determined not only by the ferromagnet but also by their intrinsic paramagnetism.

Using the values of H_{eff} given in Table II and the values of μH_{eff} obtained previously [2] in experiments on the γ anisotropy of radioactive Ir^{192}, we determine the magnetic moment of the latter. For Ir^{192}, $\mu H_{eff} = (1.2^{+0.2}_{-0.12}) \times 10^{-17}$ erg was calculated assuming spin 4.[8] For the magnetic moment we have $1.8^{+0.6}_{-0.5}\,\mu_n$.

4. ESTIMATION OF ERRORS

The principal errors and the sources of experimental error are:

a) The destruction of thermal equilibrium between the cold pipe and the mixture during a heating pulse. Excess heating of the cold pipe was measured in control runs without alloy samples. Delayed heating of the mixture (thermometer) after the heating field was switched off did not exceed 2% of the total unbalance amplitude. It can be shown that the resulting error of γ_n did not exceed ±5%.

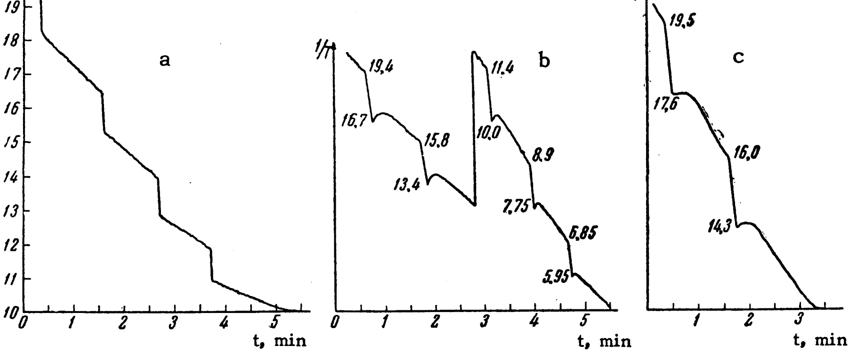

FIG. 3. Experimental curves of 1/T as a function of time for pure iron (a, sample No. 1 of Table I), metallic cobalt (b, sample No. 4 of Table I), and Fe-Ir (c, sample No. 6 of Table I). In a the reciprocal temperature is the ordinate. Figures b and c show the reciprocal temperatures at the beginning and end of a heating pulse. Figure b clearly shows how the ratio between the specific heats of the nuclear and electronic stages decreases with rising temperature. The vertical straight line following the second cycle in b corresponds to the changed balancing point of the self-induction bridge. The nuclear specific heats of samples Nos. 4 and 6 were 12 T^{-2} and 7 T^{-2} erg/deg.

Table II. Effective magnetic fields

No. of sample	μ for stable isotopes*, μ_n	μH_{eff}, erg $\times 10^{18}$	$10^5 \times H_{eff}$, Oe	
			Present work	Other investigations
5	$0,17 \pm 0,02$	$11,5 \pm 1,2$	13.5 ± 3	
6	$0,17 \pm 0,02$	11.3 ± 1.2	$13,3 \pm 3$	
7	$3,164$	$10,6 \pm 1.1$	$6,7 \pm 0,7$	$6.1 \pm 0,35$ [7]

*Mean values allowing for isotopic composition are given.

b) The thermal resistances of the cold pipe and of its contact with the sample. Appreciable values of these resistances would destroy equilibrium within the electronic stage during heat pulses. The nuclear specific heats calculated from (2) would in this case be inaccurate, the error increasing with the contributions made by the electronic specific heats of the sample and cold pipe to the total specific heat.

For Fe-Co samples Nos. 2 and 3, the electronic specific heats of which differ by a factor of 7, we would in this case obtain different results, especially above 0.1°K. The good agreement of the data in this entire temperature range shows that the aforementioned thermal resistances do not affect the specific heat measurements.

c) An error in determining the constant τ_{0e}; this constant can be obtained in principle from the thermal equilibrium curve following heating pulses (Figs. 3b and c), but with insufficient accuracy. The error is associated with the relatively large time lag of the apparatus (especially for small changes of the reciprocal temperature) and with the relatively large natural heat flow.

To calculate τ_{0e} (Sec. 1) we used data obtained in measurements with three different heating periods. The values vary from 0.4 sec-deg for C and its alloys to 0.75 sec-deg for Ir-Fe, but are identical for different samples containing the same alloying element. The specific-heat measuring errors resulting from the destruction of equilibrium during heating lead to the following errors of τ_{0e}: ±3% for Fe-Co, and ±7% for Fe-Re and Fe-Ir. These values of τ_{0e} are considerably greater than those obtained for ferromagnets by the nuclear resonance method. The method of determining the relaxation time does not permit a confident statement that τ_{0e} characterizes the nuclear relaxation process. We therefore do not consider it possible at present to compare τ_{0e} with the theory or with other experimental data. However, the values of τ_{0e} differ greatly for the various alloys and we can evidently not expect a great departure of the nuclear relaxation times from the obtained values of τ_{0e}.

An analysis of the errors shows that the experimental accuracy did not reach its limit and can be improved considerably. Our value of H_{eff} for Fe-Re agrees within experimental error with the results in [7] (Table II). It should be noted that the indicated errors pertain to Fe-Re containing 10 at.% Re, whereas our Fe-Re alloy contained 0.15 at.% Re.

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