Heat Capacity in the Normal and Superconducting States and Critical Field of Tantalum*†

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The heat capacity of a vacuum-annealed sample of tantalum has been measured in the normal and superconducting state from 1.3 to 25°K. In the normal state the heat capacity C_N can be represented by the expression $C_N=0.00136T+464.4(T/\theta)^3$, where θ varies from approximately 255 degrees at the lowest temperature to 220 degrees at the highest. The zero-field transition temperature, T_c, and the critical field H_c were determined using a calorimetric method. T_c was found to be 4.39°K. The width of the transition was approximately 0.03°C. The measured critical field was within experimental error comparable to that calculated from the heat-capacity data. The tantalum sample therefore exhibited the properties of an ideal superconductor characteristic of the so called soft superconductors. The critical field at the absolute zero, from an extrapolation of the critical field data, was found to be 780 gauss.

INTRODUCTION

THE heat capacity, critical field, and zero-field transition temperature of tantalum has been the subject of considerable research in the past.[1] The result of these investigations indicates that there is considerable disagreement in the above mentioned properties of tantalum. Furthermore there exists a discrepancy between the critical field determined from heat-capacity data and that obtained from direct determination. One of the difficulties arises from the fact that tantalum is a so-called hard superconductor whose properties (especially the magnetic properties) are very strongly dependent on the physical and chemical state of the sample. One of the methods which has been employed to reduce these hard superconductors to an ideal state has been vacuum annealing. In the case of niobium, which has been discussed in the preceding paper,[2] it was found that vacuum annealing at elevated temperatures did not result in an ideal superconductor even though the discrepancy between the calorimetric and magnetic properties was considerably diminished. It was felt, in this case, that the discrepancy persisted mainly because of the large amount of tantalum impurity which could not be removed.

An effort has therefore been made in this investigation to determine whether if, by starting initially with a tantalum sample of high purity, it could be reduced to a so-called ideal superconductor by vacuum annealing, thus removing the existing discrepancies between the calorimetric and magnetic properties.

The apparatus, procedures, treatment of data, and probable errors in the research are identical to those discussed in detail in the investigation of the heat capacity and critical field of niobium by the same authors.[2] Only those features specific to the investigation will be given below.

PURITY AND TREATMENT OF SAMPLE

The tantalum sample was obtained from Fansteel Metallurgical Corporation, the only commercial source of high-purity tantalum. The stated purity was 99.9% or better.

The tantalum sample in the form of a cylinder $\frac{3}{4}$ in. diameter and $1\frac{1}{2}$ in. long, threaded at one end was degassed and annealed before use in the calorimetric and magnetic investigations. The vacuum furnace used was identical to that used for niobium.[2] The tantalum sample was subjected to temperatures of from 1800 to 2400°C for twenty hours. The pressure of the residual gas in the furnace during this time ranged from 1×10^{-5} to 1×10^{-6} mm Hg. The final weight of the tantalum was 169.43 g which corresponded to 0.9367 mole.

EXPERIMENTAL RESULTS

1. Heat Capacity

The heat-capacity data of tantalum in the normal and superconducting states as well as some data in the intermediate state are given in Table I. The results are plotted in Figs. 1 and 2. The data in the liquid helium range are given in terms of both the 1948 temperature scale (T_{48})[3] and the 1955 temperature scale (T_{55E}).[4]

Four series of heat capacity measurements were made in the presence of a magnetic field. In the first

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[1] W. H. Keesom and M. Desirant, Physica **8**, 273 (1941); J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937); K. Mendelssohn, Nature **148**, 316 (1941); M. Desirant, *Report of the International Conference on Fundamental Particles and Low Temperatures* (Physical Society, London, 1947), Vol. 2, p. 124; W. Meissener and H. Frang Z. Physik **63**, 558 (1930); R. T. Webber, Phys. Rev. **72**, 1241 (1947); Brukseh, Zeigler, and Hickman, Phys. Rev. **62**, 354 (1942); Silsbee, Scott, and Brickwedde, J. Research Natl. Bur. Standards **18**, 295 (1937); Worley, Zemansky, and Bourse, Phys. Rev. **99**, 447 (1955).

[2] Chou, White, and Johnston, preceding paper [Phys. Rev. **109**, 788 (1958)].

[3] H. van Dijk and D. Schoenberg, Nature **164**, 41 (1949).

[4] Clement, Hogan, and Gaffney, Phys. Rev. **100**, 743 (1944).

TABLE I. Heat capacity of tantalum.

(a) Zero external field

T_{55E} (°K)	C_{55E} (cal deg^{-1} mole^{-1})	T_{48} (°K)	C_{48} (cal deg^{-1} mole^{-1})
1.255	0.00057	1.253	0.00058
1.380	0.00057	1.381	0.00056
1.379	0.00064	1.381	0.00062
1.448	0.00072	1.450	0.00070
1.650	0.00119	1.656	0.00120
1.676	0.00128	1.680	0.00129
1.875	0.00192	1.878	0.00197
1.884	0.00192	1.887	0.00197
2.055	0.00241	2.055	0.00246
2.068	0.00268	2.068	0.00272
2.209	0.00324	2.208	0.00326
2.253	0.00349	2.252	0.00349
2.404	0.00438	2.403	0.00437
2.872	0.00680	2.870	0.00690
3.200	0.00909	3.195	0.00915
3.442	0.01081	3.437	0.01079
3.726	0.01298	3.722	0.01288
3.959	0.01490	3.957	0.01470
4.109	0.01613	4.110	0.01591
4.256	0.01742	4.259	0.01721
4.441	0.01181	4.445	0.01172
4.683	0.00964	4.688	0.00958
4.926	0.01043	4.932	0.01041
5.168	0.01117	5.174	0.01119
5.702	0.01330	5.707	0.01336
6.266	0.01587	6.269	0.01586
6.732	0.01837	6.735	0.01839
7.365	0.02270	7.366	0.02280

T (°K)	C (cal deg^{-1} mole^{-1})	T (°K)	C (cal deg^{-1} mole^{-1})
8.063	0.02853	11.828	0.08054
8.698	0.03485	12.515	0.09337
8.915	0.03749	13.041	0.1047
9.365	0.04299	13.098	0.1061
9.487	0.04363	13.293	0.1110
9.899	0.04927	13.864	0.1250
10.447	0.05652	14.653	0.1464
10.490	0.05742	15.443	0.1692
11.152	0.06765	16.347	0.1994
11.577	0.07473	17.317	0.2347
11.700	0.07744	18.353	0.2753
18.988	0.3089	22.040	0.4692
19.386	0.3264	23.247	0.5573
20.611	0.3864	24.323	0.6301
21.941	0.4645		

(b) External field 1930 gauss

T_{55E} (°K)	C_{55E} (cal deg^{-1} mole^{-1})	T_{48} (°K)	C_{48} (cal deg^{-1} mole^{-1})
1.421	0.00204	1.422	0.00203
1.545	0.00222	1.551	0.00217
1.714	0.00248	1.720	0.00252
1.966	0.00280	1.967	0.00286
2.274	0.00354	2.274	0.00354
2.655	0.00421	2.654	0.00425
3.126	0.00509	3.122	0.00515
3.500	0.00604	3.495	0.00603
3.851	0.00693	3.848	0.00685
4.269	0.00829	4.271	0.00819
4.685	0.00940	4.690	0.00935
5.025	0.01059	5.031	0.01057
5.392	0.01189	5.397	0.00195

(c) External field 237 gauss

1.553	0.00101	1.558	0.00099
1.755	0.00155	1.761	0.00158
1.960	0.00224	1.962	0.00229
2.185	0.00319	2.184	0.00322
2.409	0.00431	2.408	0.00430
2.620	0.00535	2.619	0.00540
2.842	0.00660	2.840	0.00669
3.067	0.00804	3.064	0.00814
3.242	0.00940	3.238	0.00945
3.403	0.01400	3.399	0.01399
3.539	0.03356	3.536	0.03338
3.824	0.01040	3.822	0.01030
4.232	0.00816	4.234	0.00805
4.519	0.00891	4.523	0.00885

(d) External field 454 gauss

T_{55E} (°K)	C_{55E} (cal deg^{-1} mole^{-1})	T_{48} (°K)	C_{48} (cal deg^{-1} mole^{-1})
1.334	0.00104	1.334	0.00101
1.500	0.00143	1.505	0.00139
1.648	0.00181	1.654	0.00182
1.796	0.00225	1.801	0.00230
1.954	0.00284	1.956	0.00291
2.123	0.00359	2.122	0.00364
2.299	0.00457	2.298	0.00457
2.446	0.00548	2.445	0.00547
2.586	0.00712	2.584	0.00718
2.707	0.01521	2.705	0.01540
2.844	0.01411	2.842	0.01430
3.033	0.00509	3.030	0.00516
3.254	0.00560	3.250	0.00563

(e) External field 557 gauss

1.583	0.00246	1.589	0.00242
1.875	0.00347	1.879	0.00356
2.144	0.00494	2.143	0.00501
2.285	0.00724	2.284	0.00724
2.335	0.01140	2.334	0.01139

case, 1930 gauss, the sample was cooled down to the lowest temperature after which the field was applied. This field was sufficient to completely destroy the superconductivity. In the second case, 237 gauss, the field was also applied after the sample had been cooled down in zero field. This field was insufficient to destroy the superconductivity at the lowest temperatures. The superconducting transition begins to take place at approximately 3.3°K. Since the sample has the shape of a short cylinder, its demagnetizing factor causes the latent heat of transition to spread over a finite temperature as can be seen in Fig. 1. For the measurements in fields of 454 and 557 gauss, the sample was cooled down in the presence of fields of 237 and 454 gauss, respectively. It can be seen that the heat-capacity values, in these cases, are intermediate between that of the normal and superconducting state (Fig. 1). The probable explanation of this "frozen in" flux effect is that the demagnetizing effect causes an inhomogeneous field distribution around the specimen. Thus a ring on the surface of the tantalum is able to become superconducting earlier than the rest of the sample as the temperature is being reduced in a constant external field. For further variation of the field distribution a

persistent current is induced in this ring thus keeping the flux constant in the interior regions and preventing them from becoming superconducting again. A detailed discussion of the effect can be found in the literature.[5]

2. Critical Field

The zero-field transition temperature and the critical field data for tantalum are given in Table II and Fig. 3.

The zero-field transition temperatures and critical field were determined from heating curves previously discussed in detail.[2] From these curves the zero-field transition interval has been estimated as 0.03°C. The temperature given in Table II corresponds to those

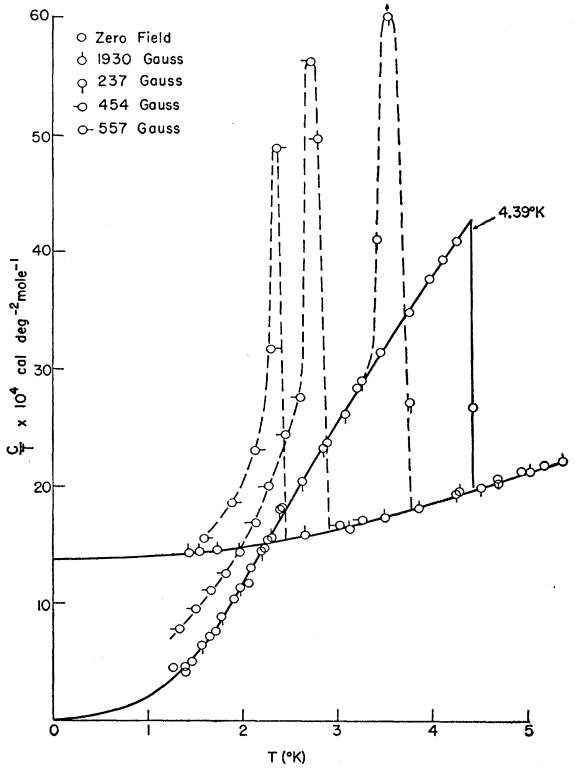

FIG. 1. Heat capacity of tantalum in various external magnetic fields.

temperatures at which the superconductivity was completely destroyed. This can be readily ascertained by comparison with the heat-capacity measurements in fields insufficient to destroy the superconductivity.

DISCUSSION OF RESULTS

1. Heat of Capacity

The heat capacity of a superconductor in the normal state C_N, at low temperatures, can be expressed by the Debye-Sommerfeld relation as the sum of an electronic

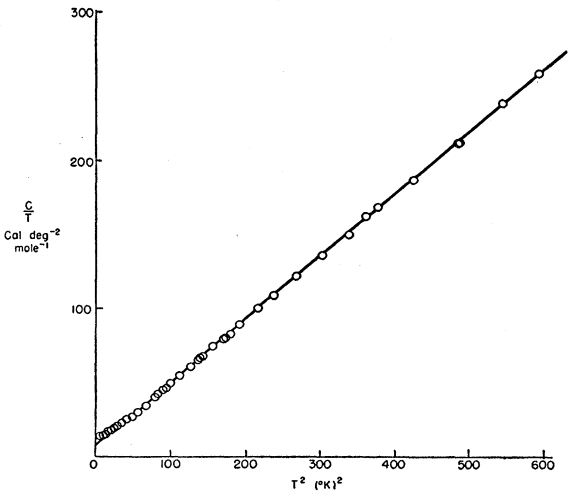

FIG. 2. Heat capacity of tantalum in the normal state.

and lattice term

$$C_N=\gamma T+464.4(T/\theta)^3.$$

As in the case of niobium,[2] it is found that Debye θ for tantalum is not a constant but varies with temperature. This is consistent with theoretical calculations of Fine.[6] Since there is considerable uncertainty in the theoretical form of the variation of θ with temperature, the electronic specific heat constant, γ, cannot be evaluated readily from the heat capacity data. The contribution of the lattice to the total heat capacity cannot be neglected even for the determinations at the lowest temperatures. A numerical extrapolation procedure was therefore used to estimate γ. It was found to be $(13.6\pm0.3)\times10^{-4}$ cal mole^{-1} deg^{-2}. Upon using this value of γ, the variation of Debye θ with temperature is shown in Fig. 4.

A comparison of the heat capacity of tantalum in the normal and superconducting states from this

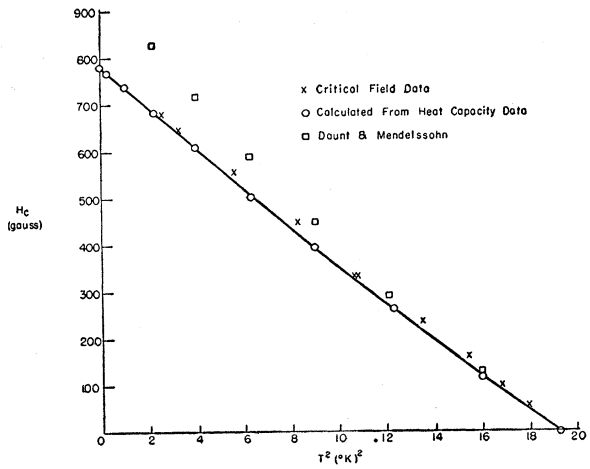

FIG. 3. Critical field of tantalum.

[5] D. Shoenberg, *Superconductivity* (Cambridge University Press, New York, 1952), second edition.

[6] P. C. Fine, Phys. Rev. **56**, 355 (1939).

TABLE II. Critical magnetic field of tantalum.

T_{55E} (°K)	T_{43} (°K)	H (gauss)
4.390	4.393	0
4.237	4.239	56
4.111	4.112	100
3.929	3.927	160
3.675	3.670	237
3.288	3.282	336
3.272	3.266	337
2.884	2.881	454
2.354	2.353	557
1.798	1.802	647
1.608	1.614	683

research with earlier results has already been made by Worley *et al.*[1] and will not be discussed further here.

2. Calculation of the Critical Field of Tantalum from the Heat-Capacity Data

The critical magnetic field H_c as a function of temperature can be determined from the heat capacity by using the following expression:

$$H_c^2=\frac{-8\pi}{V}\int_T^{T_c}\left\{\int_0^T\left(\frac{C_n-C_s}{T}\right)dT\right\}dT,$$

where V, T_c, and C_s are the molar volume, the zero-field transition temperature, and the heat capacity in the superconducting state, respectively. The term in the curly brackets corresponds to the difference in entropy, ΔS, between the normal and superconducting states. The molar volume of tantalum was estimated to be 10.83 cc mole^{-1} for 0–5°K. The critical field calculated from the above equation as well as ΔS is given in Table III.

The above tabulated critical fields are also shown in Fig. 3. The initial slope of the critical field $(dH_c/dT)_{T=T_c}$ and the critical field at the absolute zero are -331 ± 2 gauss deg^{-1} and 780 ± 4 gauss, respectively. The initial slope calculated from the difference in heat capacity, ΔC, between the normal and superconducting state at the zero field transition temperature, using the Rutgers' equation

$$\Delta C=0.01010=(-VT_c/4\pi)(dH_c/dT)_{T=T_c}^2$$

gives a value of -334 ± 2 gauss deg^{-1}. The values of $(dH_c/dT)_{T=T_c}$ and H_0 reported recently by Worley, Zemansky, and Bourse[1] from their calorimetric data are -334 gauss deg^{-1} and 860 gauss, respectively.

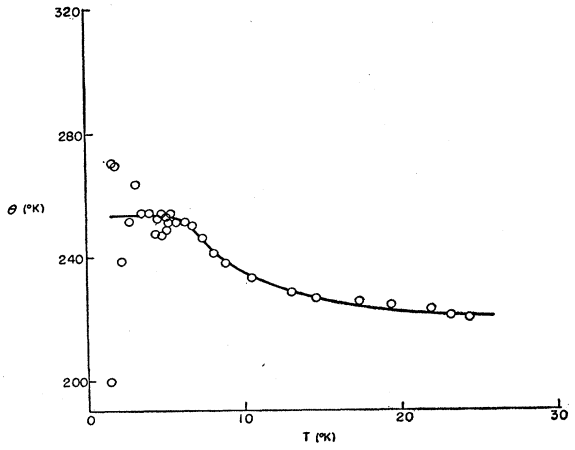

FIG. 4. Debye θ as a function of temperature for tantalum.

3. Comparison of Measured Critical Field with That Calculated from Heat-Capacity Data

A comparison of the experimentally determined critical field of tantalum with that calculated from the heat-capacity data is shown in Fig. 3. The agreement is quite striking and indicates that the annealing has reduced the tantalum to an ideal superconductor. The experimentally determined critical field fits the parabolic relationship given below, within experimental error.

$$H_c=780\{1-(T/4.39)^2\}. \quad (1)$$

The initial slope calculated from the relationship is -355 gauss deg^{-1} and the critical field at the absolute zero is 780 gauss. The data of Daunt and Mendelssohn[1] are also shown in Fig. 3. Their critical field at the absolute zero, 975 gauss, and the slope of the critical field curve at T_c, -310 gauss are considerably higher than the values obtained in this research. For a well-annealed sample free of internal strain, both H_0 and $-(dH/dT)_{T=T_c}$ will be lower than for an unannealed sample. Since our calorimetric results yield the same critical field curve, within experimental error, as that measured, it can be assumed that the tantalum sample was in a so-called "ideal" state characteristic of the soft superconductors. This would imply that the frozen internal strain in our sample was very small. Nevertheless $-(dH/dT)_{T=T_c}$ calculated from either our calorimetric data or the parabolic relation given above, is considerably higher than that reported by Daunt and Mendelssohn.

Another method which can be used to check the consistency between the heat-capacity data and the critical field data is by comparison of the latent heat of the superconducting transition in a field of 237 gauss.

TABLE III. Critical field as a function of temperature.

T (°K)	$\Delta S\times10^4$ (entropy units)	H_c (gauss)
0.0	0.00	780
0.5	6.50	769
1.0	13.08	738
1.5	18.31	683
2.0	21.23	609
2.5	21.48	504
3.0	19.03	395
3.5	14.22	259
4.0	7.20	115
4.39	0.00	0

The latent heat Q in a field of 237 gauss at the transition temperature of 3.67°K can be computed from the parabolic relation (1) representing the critical field data from the expression

$$Q=-VT(H_c/4\pi)(dH_c/dT)$$
$$=0.0053_2 \text{ cal mole}^{-1}.$$

The latent heat at the above transition temperature and critical field cannot be calculated from the heat-capacity data without making some assumptions since the demagnetization factor due to the shape of the sample causes the transition to spread over a finite temperature range (Fig. 1). However, the change in enthalpy, ΔH, from 3.24°K (in the superconducting state) to 4.24°K (in the normal state) determined from the heat-capacity data in a field of 237 gauss,

$$\Delta H=\int_{3.24}^{4.24} C_{237 \text{ gauss}}dT=0.0145 \text{ cal mole}^{-1},$$

can be compared with the change in enthalpy over the same temperature range from the following expression:

$$\Delta H=\int_{3.24}^{3.67} C_s dT+Q+\int_{3.67}^{4.24} C_n dT,$$

where Q is determined from the critical field data. Using the value of Q obtained above, $\Delta H=0.0143$ cal mole^{-1}, which is in good agreement with the value obtained from the calorimetric data.

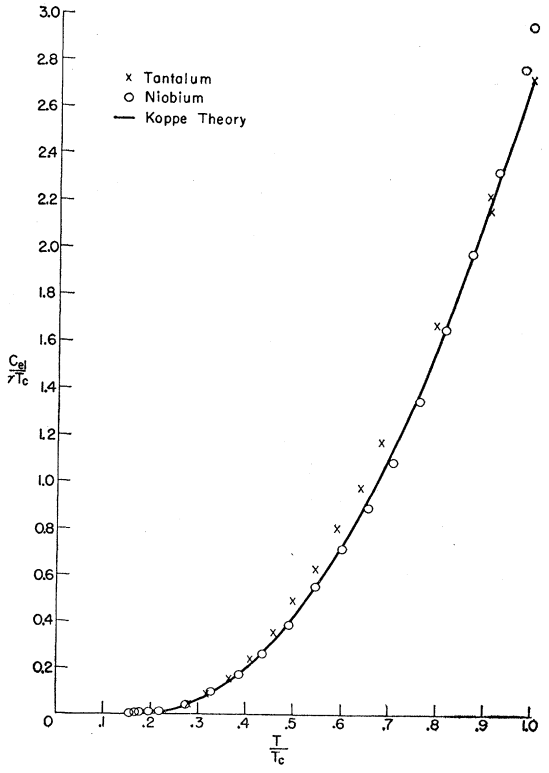

FIG. 5. Comparison of the heat capacity of tantalum and niobium with corresponding state theory of Koppe.

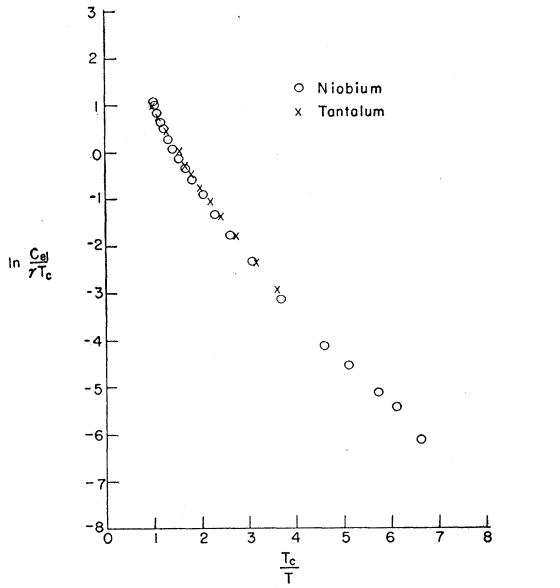

FIG. 6. Comparison of the heat capacity of tantalum and niobium with relation of Corak *et al.*

4. Comparison of Heat-Capacity Data with Corresponding State Theories of Superconductivity

The experimental heat-capacity data have been compared with two theoretical calculations, one by Marcus and Maxwell[7] and the other by Koppe,[8] which relate $C_{el}/\gamma T_c$ to the dimensionless quantity, T/T_c, for all superconductors. C_{el} is the electronic contribution to the heat capacity in the superconducting state and was computed from the expression

$$C_{el}=C_s-C_n+\gamma T.$$

The agreement with the α theory of Marcus and Maxwell is poor. A comparison of the smoothed heat-capacity data with the theoretical curve predicted by Koppe can be seen in Fig. 5. The heat capacity results for niobium[2] have also been included.[9] The agreement with the niobium heat capacities appears to be better than that for tantalum; however, even for niobium the deviations at the lowest temperature are quite considerable.

[7] P. M. Marcus and E. Maxwell, Phys. Rev. **91**, 1035 (1953).
[8] H. Koppe, Ann. Physik **1**, 405 (1947).
[9] The value of γ used in the computation of C_{el} for niobium was 19.0×10^{-4} cal mole^{-1} deg^{-2}. This value was chosen to avoid negative values of C_{el} at the lowest temperatures, which would result if the more probable value of $\gamma=18.0$ cal mole^{-1} deg^{-2} is used. Although the heat-capacity data at the lowest temperatures are subject to considerable uncertainty and may give rise to this effect, another possibility is that the generally accepted assumption that the heat capacity of the superconducting state is the *sum* of two terms, lattice and electronic, may be invalid.

The heat-capacity data for both tantalum and niobium have also been compared with the empirical relation,

$$C_{el}/\gamma T_c = Ae^{-bT_c/T},$$

of Corak, Goodman, Satterthwaite, and Wexler.[10]

The data for niobium and tantalum appear to be on the same curve, Fig. 6. However, it is evident that there is considerable deviation from the straight line predicted, particularly at the lowest temperatures.

[10] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102** 656 (1956).

ACKNOWLEDGMENTS

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Remarks on the Volume Magnetostriction and the Anisotropic Forced Magnetostriction

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The manner in which the anisotropic forced magnetostriction contributes to the magnetostriction of ferromagnetic substances at high-magnetic fields is discussed theoretically. In the past, the isotropic forced volume magnetostriction has been considered to be the only cause of the forced magnetostriction. This is probably one reason for the discrepancies between the experimental value of the volume magnetostriction and the theoretical value expected from the pressure dependence of the Curie point, etc. In addition to this, the limitations of the present theory concerning the relation between the isotropic volume magnetostriction and the related properties mentioned above are briefly examined in connection with the discrepancies between experiment and theory.

I. INTRODUCTION

IT is generally accepted that there are two completely different kinds of magnetostriction corresponding to the two magnetization processes. The first is one corresponding to the magnetization process of alignment of domain magnetization vectors while the second involves an increase in the spontaneous magnetization of the domain itself.

In the alignment process the domian magnetization vectors change their direction; the crystallographic orientation remaining fixed. It should therefore be possible to explain the magnetostriction curves by assuming that below the Curie temperature all the domains are spontaneously strained by the spontaneous magnetization within each domain. The strain within each domain is assumed to vary with the direction of the domain magnetization. Therefore, as the domain distribution changes with the magnetization, magnetostriction occurs and this should saturate when the magnetization saturates. Furthermore, there is only a very small volume change when the domain magnetization changes from one crystallographic direction to the other. This type of dependence of the spontaneous lattice strain can be calculated from considerations of lattice symmetry and has been treated in detail by Becker and others.[1–3] Since this part of the magnetostriction derives from the spontaneous lattice strain and a volume change is not involved, we shall call this part the "morphic term"[4] of the magnetostriction.

After the magnetization is saturated, one can still observe a change in size of a ferromagnetic sample which depends linearly upon the magnetic field. This differs from the low-field magnetostriction in that whereas the latter takes place without change of volume, the magnetostriction in a high field is primarily a volume effect, the expansion being the same in all directions. It is natural to associate this volume strain with the field-induced increase in the spontaneous magnetization. In this sense, the effect is called forced magnetostriction. Since this effect is related to the nature of the special internal forces in a ferromagnetic crystal (about which information is not obtainable by other means) it has been the object of an intense study and also is the main concern of this note.

As a matter of fact, the volume magnetostriction is usually considered to consist of three different terms which arise from different sources.[1,2] These are the form effect, the crystal effect, and the forced magnetostriction mentioned above.

The form effect arises purely from sample geometry. When the sample is magnetized, because of its finite demagnetizing factor, it has a certain amount of magnetostatic energy and magnetostriction occurs in order

[1] R. Becker and W. Döring, in *Ferromagnetismus* (Verlag Julius Springer, Berlin, 1938), pp. 270–311.
[2] E. W. Lee, in *Report on Progress in Physics* (Physical Society, London, 1955), Vol. 18, p. 184.
[3] W. P. Mason, Phys. Rev. **82**, 715 (1951).

[4] This word has been used in a different sense to describe the change in the elastic constants due to the deformation of the crystal lattice accompanying spontaneous magnetostriction.