Lawrence Berkeley National Laboratory
Recent Work

Title

LOW-TEMPERATURE HEAT CAPACITIES OF THE CLATHRATE SALTS Ag7O8NC3, AND Ag7O8HF2

Permalink

https://escholarship.org/uc/item/3zn2b29k

Authors

Conway, Mary M.
Phillips, Norman E.
Geballe, T.H.
et al.

Publication Date

1969-12-01

eScholarship.org Powered by the California Digital Library
University of California

Submitted to J. of Physics and
Chemistry of Solids

UCRL-19170
Preprint

c. 2

LOW-TEMPERATURE HEAT CAPACITIES OF THE CLATHRATE SALTS $Ag_7O_8NO_3$ AND $Ag_7O_8HF_2$

Mary M. Conway, Norman E. Phillips, T. H. Geballe, and N. A. Kuebler

RECEIVED
LAWRENCE
RADIATION LABORATORY

MAR 5 1970

LIBRARY AND
DOCUMENTS SECTION

December 1969

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-19170

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-19170

Low-Temperature Heat Capacities of the Clathrate Salts $Ag_7O_8NO_3$ and $Ag_7O_8HF_2$.*

Mary M. Conway† and Norman E. Phillips

Inorganic Materials Research Division of the Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California.

and

T. H. Geballe‡ and N. A. Kuebler

Bell Telephone Laboratories, Murray Hill, New Jersey

Abstract

The heat capacities of $Ag_7O_8NO_3$ and $Ag_7O_8HF_2$ have been measured between 0.3 and, respectively, 20 and 4°K. The measurements show that the previously reported type II superconductivity is a bulk property, and give the values of some of the normal- and superconducting-state parameters. There is a surprisingly strong dependence of the electronic density of states and Debye temperature on anion identity, but no convincing evidence for a direct effect of anion identity on T_c.

*Work at Berkeley supported by the U.S. Atomic Energy Commision; work at Stanford supported by A.F.O.S.R. Grant 68-1510B.

†National Science Foundation Graduate Fellow.

‡Also at Stanford University, Stanford, California.

INTRODUCTION

The silver-oxide clathrate salts $Ag_7O_8^+X^-$ with $X^- = NO_3^-$, HF_2^-, BF_4^-, F^- are the only known examples of clathrates that exhibit metallic conductivity. For the NO_3^- salt, residual resistance ratios, $\zeta(300°K)/\zeta(4.2°K)$, as high as 200 have been observed, and the phonon resistivity varies as $T^{3.5}$ below 12°K.[1] These salts also undergo superconducting transitions. The transition temperatures T_c, as determined by magnetic measurements, were originally reported as 0.15, 0.3, and 1.04°K for the BF_4^-, F^-, and NO_3^- salts respectively.[1] Later measurements showed that the samples of the F^- salt had contained paramagnetic impurities and that samples of the HF_2^- salt have transition temperatures of 1-1.5°K.[2]

The crystal structure is based on face-sharing, 26-sided, Ag_6O_8 polyhedra. Oxygen atoms are located at the 24 corners (each common to 3 polyhedra) and Ag atoms at the centers of the 12 square faces (out of 18) that are common to 2 polyhedra. Cubic spaces between the polyhedra, equal in number to the polyhedra, contain the one additional Ag atom per polyhedron, and the anions are located at the centers of the polyhedra. At room temperature the known salts have a face-centered cubic lattice, but the NO_3^- salt becomes face-centered tetragonal below about 180°K, with c/a = 0.9603 at 10°K. A phase change also occurs in the HF_2^- salt, at 80°K,[2] but the structure of the low-temperature form has not been established. It seems

probable that both transitions are associated with the anions taking up regular orientations in the cage. The salts with the more symmetrical F^- and BF_4^- anions apparently remain cubic at low temperature.[1] The room-temperature cubic unit cell dimensions of the HF_2^-, F^-, NO_3^-, and BF_4^- salts are 9.824, 9.833, 9.893, and 9.942 Å, respectively.[1,2]

The heat capacity measurements on $Ag_7O_8NO_3$ and $Ag_7O_8HF_2$ reported here were undertaken to verify the existence of bulk superconductivity and to obtain values of the related normal-state parameters N(0), the density of electronic states at the Fermi energy, and θ_o, the Debye characteristic temperature at 0°K. It was hoped that a comparison of these parameters and T_c for different salts might provide a basis for deciding whether or not vibrational modes associated with the loosely-bound anions played a role in determining the superconducting-state properties. The possible importance of anion vibrational modes is of course suggested by the strong variation in T_c produced by changing the anion. The NO_3^- salt was chosen for study because it showed the sharpest transition. The other three salts known to become superconducting all show broader transitions (apparently because of the presence of small amounts of a paramagnetic impurity, possibly silver ion in the d^9 configuration) and the HF_2^- salt was chosen primarily for its high transition temperature.

RESULTS

The heat capacity measurements were made on samples consisting of small crystals with dimensions on the order of a few millimeters. Thermal contact with a copper calorimeter was made with a small amount of silicone oil. The heat capacities of the calorimeter and oil were measured separately. Temperature was measured with a germanium thermometer that had been calibrated against a cerium magnesium nitrate thermometer (0.25-1°K), the 1958 He^4 vapor-pressure scale (1-4°K), and a gas thermometer (4-20°K). The results below 2°K, in several magnetic fields, are shown in Fig. 1 as C/T vs. T^2.

The heat capacity of $Ag_7O_8NO_3$ in the normal state shows the temperature dependence expected for a metal at very low temperatures,

$$C = \gamma T + (12/5)\,\pi^4 R\,(T/\theta_o)^3, \qquad (1)$$

where γ is a constant proportional to N(0). In 2400 Oe, the heat capacity of $Ag_7O_8HF_2$ includes a term proportional to T^{-2} which is believed to be a consequence of the presence of paramagnetic impurities: it would require 0.04 moles of free-electron spins per mole of $Ag_7O_8HF_2$ to produce an effect of this magnitude. The coefficient of this term was determined from the 0-°K intercept of a plot of CT^2 vs. T^3 and the T^{-2} term was subtracted from the total heat capacity to obtain the dashed line shown in Fig. 1 for $Ag_7O_8HF_2$ in the normal state.

The γ and θ_o values corresponding to the dashed lines in Fig. 1 are given in Table I. All values are calculated for the molar formula Ag_7O_8X, which corresponds to one primitive unit cell. The variation of θ with T is shown for both salts in Fig. 2.

In zero magnetic field, the heat capacity of the $Ag_7O_8NO_3$ exhibits the temperature dependence expected for a slightly broadened superconducting transition: on cooling, the transition begins at 1.046°K and is 90% complete (as estimated from the magnitude of the heat capacity) at 1.004°K. The lowest temperature zero-field data were corrected for the lattice heat capacity and fitted to the BCS expression[5] for the superconducting-state electronic heat capacity,

$$C_{es} = a\ \gamma\ T_c\ \exp\ (-bT_c/T) \qquad (2)$$

With T_c taken as 1.025°K (see below) this expression fits the data for $T_c/T > 1.7$ with a = 6.12 and b = 1.22, as shown in Fig. 3. The superconducting-state entropy, obtained by integration of the heat capacity (using extrapolated values below 0.38°K and above 0.94°K) is equal to the normal-state entropy at 1.025°K, and this temperature, which also corresponds approximately to the middle of the drop in heat capacity, has been taken as T_c. The critical magnetic field, calculated by a second integration, has a 0°K value $H_c(0)$ = 130 Oe, and a maximum deviation from parabolic temperature dependence of -6%.

The superconducting transition of $Ag_7O_8NO_3$ is shifted to lower temperatures with increasing magnetic field in the way expected for type-II superconductivity. The in-field transition occurs at the temperature at which the upper critical field $H_{c2}(T)$ is equal to the applied field. This temperature was taken as that of the midpoint of the drop in heat capacity. The three values of $H_{c2}(T)$ determined from the three heat capacities taken in magnetic fields were used to calculate the Landau-Ginsburg parameter, defined by[6] $\kappa = H_{c2}(T)/\sqrt{2}\, H_c(T)$. κ was found to be 2.2, 2.6, and 3.2 at 0.82, 0.67, and 0.58°K, respectively. These values do not fit the temperature dependence of κ predicted by the usual theories, but the discrepancy cannot be regarded as significant in view of the breadth of the transitions observed in higher mangetic fields and the resulting uncertainty in $H_{c2}(T)$.

The zero-field superconducting transition of $Ag_7O_8HF_2$ is broadened considerably, presumably by the paramagnetic impurities responsible for the T^{-2} term in the normal-state heat capacity. It seems reasonable to suppose that the transition has also been lowered by the same mechanism and that T_c for the pure salt may be considerably higher than 1.5°K. The breadth of the transition prevented an evaluation of the other superconducting-state parameters and, for the same reason, no attempt was made to study the depression of the transition in small magnetic fields.

The transition temperatures obtained for both salts are in good agreement with the values obtained from magnetic measurements,

but the values of $H_c(0)$, γ, and κ obtained for the NO_3-salt do not agree with the values obtained from magnetic measurements. Robin et al. calculated $H_c(0) = 57$ Oe from the area under a magnetization curve at 0.1°K and, with the assumption of a parabolic dependence of H_c on T, found $\gamma = 7.3$ mJ/mole-°K^2. They also estimated $K \approx 100$ from the shape of the magnetization curve. It seems clear that the values of γ and $H_c(0)$ must be given correctly by the calorimetric measurements. (Measurements on a second sample, not reported here, gave essentially identical results.) On the other hand, it is not at all clear why the magnetic measurements gave such different values. Possibly the discrepancy is related to the different physical condition of the samples: the magnetic measurements were made on powdered material and the calorimetric samples consisted of small crystals.

DISCUSSION

Substitution of an HF_2^- ion for an NO_3^- ion produces a volume contraction of only 2.1%, but increases θ_o from 85.3 to 125°K. This effect, which would correspond to a Gruneisen constant of ≈18, is an order of magnitude larger than would be expected for a pressure-induced contraction in an ordinary lattice.

With increasing temperature, there are two distinct drops in the value of θ for the NO_3^- salt. The initial drop, from 82.5°K near 0°K to ≈60°K in the 5-10°K region is typical of

that observed in many solids and is of a magnitude often associated with phonon dispersion. However, the second drop, which occurs above 15°K, is unusual. It is very probably associated with a rocking mode of the NO_3^- ion, but the lack of measurements on the HF_2^- salt in this temperature region make this interpretation somewhat speculative.

The HF_2^- salt shows only a temperature-independent paramagnetic susceptibility, and Hall-effect measurements indicate the presence of between two and three carriers per Ag_6O_8 unit. It has been suggested that the A atoms in the Ag_6O_8 units are in the diamagnetic $4d^8$ square-planar configuration, and that the two remaining electrons are in a conduction band that utilizes the 4d orbitals of the Ag atoms and the 2p orbitals of the O atoms.[2] The free-electron γ value corresponding to this electron density (which is not very sensitive to the exact number of electrons) is 4.8 mJ/mole-°K. The observed γ values are considerably higher--44.6 and 72.5 mJ/mole-$°K^2$ for the NO_3^- and HF_2^- salts, respectively--showing that N(O) is much greater than for free electrons, and suggesting that the conduction band is very narrow. Since there is very little conduction electron density at the anion,[2] the difference in N(O) between the two salts must be attributed mainly to the different Ag-O distances. The effect of lattice parameter on N(O) is also surprisingly large--a 2.1% reduction in volume is accompanied by a 62% increase in N(O).

The possibility that the anions contribute directly to the superconducting interaction in these salts can be tested by comparing the observed critical temperatures with theoretical expressions that relate T_c to normal-state properties. (The theoretical expressions also contain quantities that are not known independently, and it is necessary to rely on empirical correlations between these quantities and other properties.) The value of T_c is known accurately only for the NO_3^- salt, and we shall start from that value and estimate T_c for the pure HF_2^- salt on the assumption that in both cases the only important interactions between electrons are the coulomb repulsion and the attractive interaction via acoustic phonons. First, however, it is useful to consider the probable effect of the magnetic impurities on the critical temperature of the HF_2^- salt. On the assumption that the observed broadening of the transition is produced by magnetic impurities, the value of T_c for the pure HF_2^- salt must be at least 1.5°K, the highest temperature at which the zero-field heat capacity deviates from the normal-state value. A theoretical treatment,[7] which has been partially confirmed by experimental data,[8,9] predicts an approximately linear decrease in the energy gap and in T_c with increasing concentration of paramagnetic impurities, for concentrations that are not too high. The fractional decrease in the energy gap is approximately double the fractional decrease in T_c for the same impurity concentration. The theory is not sufficiently complete to allow a detailed comparison with the superconducing-state heat capacity of the

HF_2^- salt. However, the lowest-temperature zero-field heat capacity data for the HF_2^- salt show a sharp drop with decreasing temperature suggesting the presence of a significant energy gap and T_c for the pure material is therefore unlikely to be higher than about 5°K.

The BCS theory[5] represents the phonon spectrum and the electron-electron interactions by single parameters--θ_o and V, respectively--and gives the critical temperature as

$$T_c = 0.855\ \theta_o \exp[-1/N(0)V]. \qquad (3)$$

The values of V deduced by application of this equation to experimental values of T_c, θ_o, and N(0) vary considerably from one superconductor to another. However, if the numerical coefficient 0.855 is replaced by an adjustable parameter, the experimental data for a number of alloy systems are adequately represented by Eq. (3) with constant values of V.[10] The adjustable parameter usually assumes a value closer to 0.4 or 0.5. (The theory employs several approximations that might be related to this discrepancy, one of which is the use of Debye spectrum to relate the average phonon frequency to θ_o. For a typical solid the average frequency would be lower relative to θ_o and the correct value of the numerical coefficient would therefore be somewhat less than 0.855.) If it is assumed that V has the same value for the NO_3^- and HF_2^- salts, T_c for the HF_2^- salt can be predicted from that of the NO_3^- salt and the various normal-state parameters. Using Eq. (3), the predicted T_c for the HF_2^- salt is 7.8°K, and, if the numerical coefficient is changed to 0.4, the predicted T_c becomes 5.8°K. Thus, the T_c

of pure $Ag_7O_8HF_2$ does not appear to differ significantly from the value expected from the T_c of $Ag_7O_8NO_3$ and the normal-state parameters.

McMillan[11] has given a more exact treatment of the electron-electron interactions, and derived, for the critical temperature,

$$T_c = 0.69\ \theta_o \exp\left[-\frac{1.04(1+\lambda)}{\lambda - u^*(1+0.62\lambda)}\right]. \qquad (4)$$

In the derivation, a particular phonon spectrum (that of niobium) was assumed but the result is expected to be valid for all weak-coupling ($\lambda < 1$) superconductors. The coulomb-repulsion u^* is approximately 0.10 for simple metals and 0.13 for transition metals. The attractive phonon interaction λ is proportional to the "bare" or band-structure density of states, $N_{bs}(0) = N(0)/(1+\lambda)$, and for certain alloy systems $N_{bs}(0)$ seems to dominate the dependence of λ on concentration.[12] (The dominance of the $N_{bs}(0)$ factor is closely related to the validity of Eq. (3) with a constant V and modified numerical factor.) A comparison of the critical temperatures of $Ag_7O_8NO_3$ and $Ag_7O_8HF_2$ on the basis of Eq. (4) and the assumption that λ is dominated by $N_{bs}(0)$ is very similar to that based on Eq. (3). With $u^* = 0.13$, and T_c for the HF_2^- salt taken as

the highest observed value, 1.5°K, λ has the same value for both salts--0.57. If λ were proportional to $N_{bs}(0)$ the values of λ and T_c for the HF_2^- salt would be larger relative to those for the NO_3^- salt--0.81 and 4°K, respectively--but the discrepancy is not large enough to be significant.

Although some data indicates that λ is proportional to $N_{bs}(0)$, McMillan has suggested, on the basis of other empirical evidence, that the dependence on $N_{bs}(0)$ is cancelled by other factors in λ and that within a given class of superconductors λ is inversely proportional to the square of a certain average of the phonon frequencies.[11] On this basis the values of λ and T_c for the HF_2^- salt would be predicted to be much lower relative to the values for the NO_3^- salt--0.27 and 10^{-3}°K, respectively. This would suggest that the superconducting interaction in the HF_2^- salt is in some way enhanced over that in the NO_3^- salt. However, the correlation on which this comparison is based is not well established--the number of examples that have been found to support it is small, and its role in those cases in which λ is proportional to $N_{bs}(0)$ is not clear.

CONCLUSION

The previously reported superconductivity of $Ag_7O_8NO_3$ and $Ag_7O_8HF_2$ is a bulk property. All samples of the HF_2^- salt that have been investigated so far have probably contained enough magnetic impurities to depress the critical temperature, and the critical temperature of pure material is probably higher than 1.5°K, but less than 5°K.

The electronic density of states and the phonon frequencies of the silver oxide cage structure are extremely sensitive to the changes in lattice parameter associated with changes in anion size. Apart from this indirect effect, there is a yet no clear indication that the anion plays any role in the superconductivity of these salts.

REFERENCES

1. M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, and D. B. McWhan, Phys. Rev. Letters, 17, 917 (1966).
2. A. C. Gossard, D. K. Hinderman, M. B. Robin, N. A. Kuebler, and T. H. Geballe, J. Amer. Chem. Soc. 89, 7121 (1967).
3. Chou Kung-Du, Scientia Sinica 12, 139 (1963).
4. I. Náray-Szabo, G. Argay, and P. Szabo, Acta. Crystallogr. 19, 180 (1965).
5. J. Bardeen, L. Cooper, and J. R. Schieffer, Phys. Rev. 108, 1175 (1957).
6. A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [English transl: Soviet Phys.--JETP 5 1174 (1957)]; J. Phys. Chem. Solids 2, 199 (1957).
7. S. Skalski, O. Betheder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).
8. M. A. Woolf and F. Reif, Phys. Rev. 137, A557 (1965).
9. D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. 137, A550 (1965).
10. See, for example, E. Bucher, F. Heiniger, J. Muheim, and J. Muller, Rev. Mod. Phys. 36, 146 (1964).
11. W. L. McMillan, Phys. Rev. 167, 331 (1968).
12. See Fig. 9 of Ref. 11.

Table I

Normal- and superconducting state parameters of $Ag_7O_8HF_2$ and $Ag_7O_8NO_3$.

	γ (mJ/mole-°K^2)	θ_o (°K)	T_c (°K)	$H_c(0)$ Oe
$Ag_7O_8HF_2$	72.5	125	0.8-1.5	
$Ag_7O_8NO_3$	44.6	85.3	1.025	130

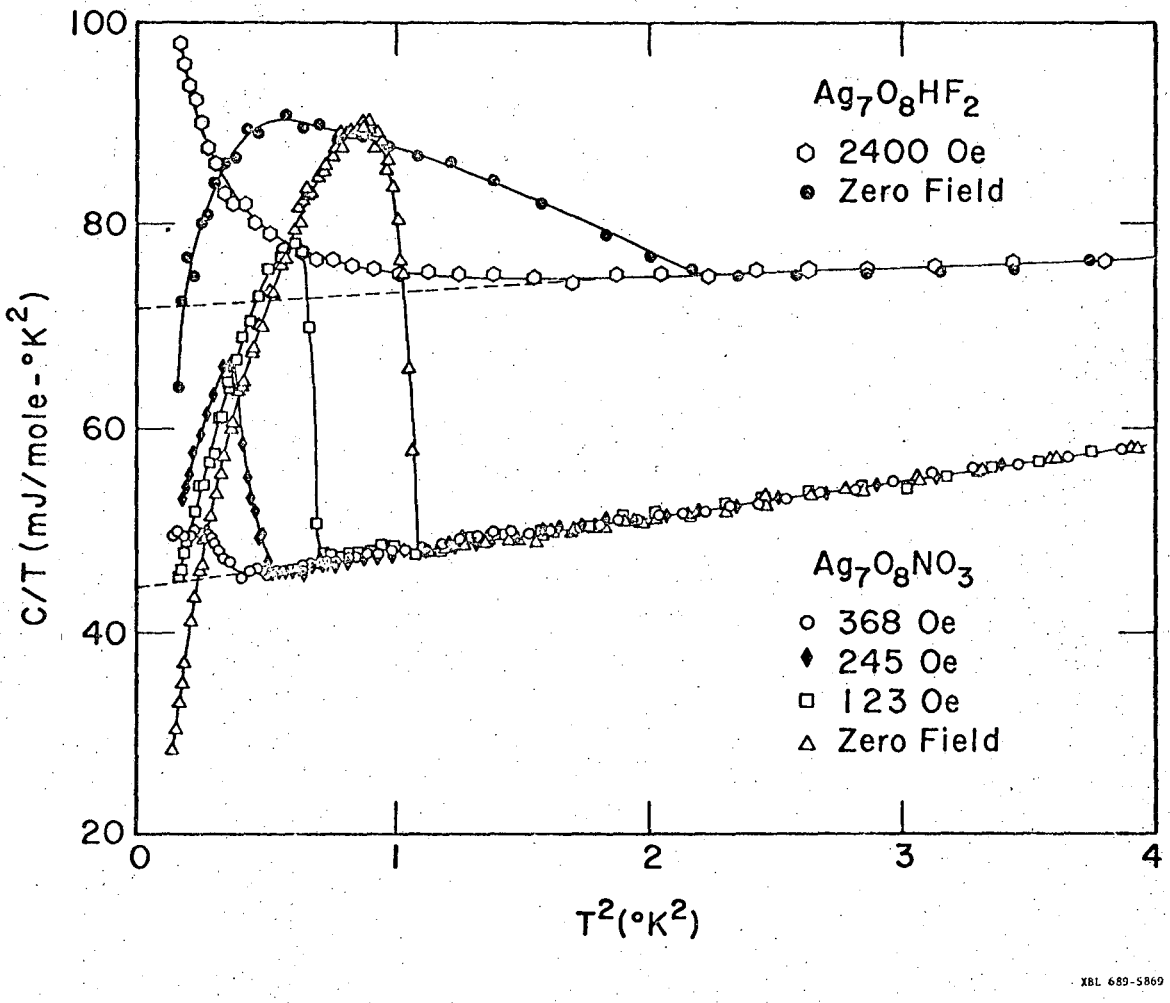

Figure 1. The heat capacities of $Ag_7O_8HF_2$ and $Ag_7O_8NO_3$. Only the data for $T < 2°K$ are shown.

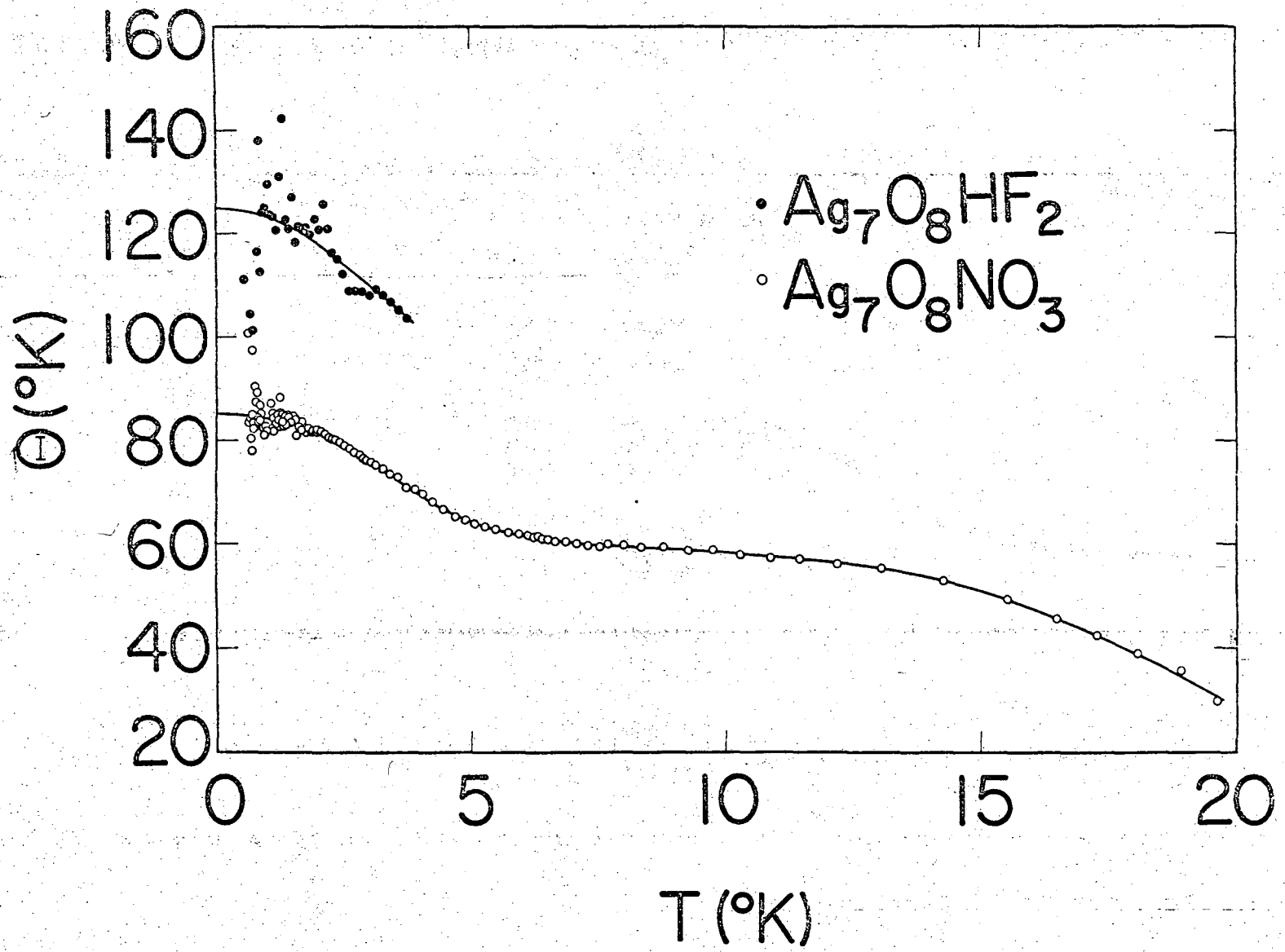

Figure 2. The Debye characteristic temperatures of $Ag_7O_8HF_2$ and $Ag_7O_8NO_3$. XBL 689-5870

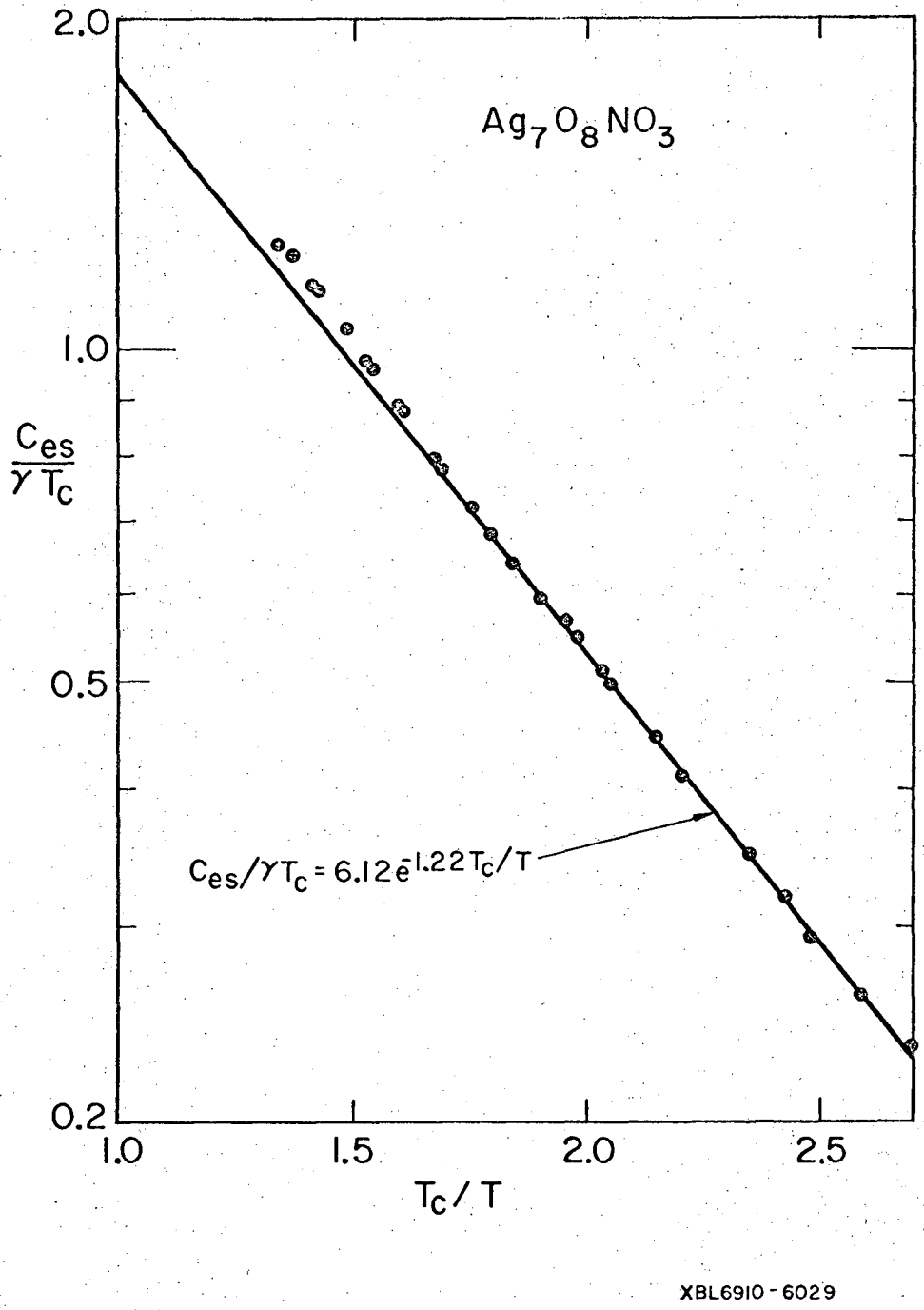

Figure 3. The superconducting-state electronic heat capacity of $Ag_7O_8NO_3$.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720