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STUDY OF TRANSITION TEMPERATURES IN SUPERCONDUCTORS

by

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I. Introduction

Our effort continues to be centered around the density of states model for β-W superconductors. The current situation is summarized in the appendix to this report, which was presented in August at the Eleventh International Conference on Low Temperature Physics.

Research in progress falls into three main areas: extension of the band model to additional behavior (theoretical and experimental work on the transport properties of Nb_3Sn); probing the extent of the validity of the model by both physical (stress dependence of T_c) and chemical (doping) experiments; and searching for possible interactions needed to remedy certain deficiencies in the theory (neutrons diffraction, magnetic field dependence of the elastic constants). In addition, work continues on the attempted growth of large single crystals of Nb_3Sn.

II. Recent Progress

A. Theory
(R. W. Cohen)

The electrical resistivity in the tetragonal lattice state has been calculated according to the two band model for Nb_3Sn. The theory predicts a drop of several per cent in the magnitude of the resistivity at the transformation temperature T_m. For temperatures below T_m, the phonon contribution to the resistivity ρ_{ph} decreases faster than the corresponding cubic state values. At sufficiently low T, we find $\rho_{ph} \propto T^{3.2}$ for the tetragonal state, compared to $\rho_{ph} \propto T^{2.7}$ for the cubic state. For an ordinary two band transition metal, one finds ordinarily $\rho_{ph} \propto T^3$. A detailed comparison of the theory and experiment should provide important information as to whether the electron-phonon interaction, which is responsible for superconductivity, changes when the crystal transforms from

the cubic to the tetragonal state.

A calculation of the temperature dependence of the thermoelectric power Q is underway. Preliminary results indicate a peak in Q. According to the β-W band model, the peak ought to come at the temperature at which the Fermi level crosses the d band edge ($\sim$ 110°K), so that a verification of this prediction provides another important test of our ideas on the β-W band structure.

B. Measurement

1. Transport Properties
(R. W. Cohen and G. Gunsalus)

The Hall coefficient, thermoelectric power, and resistivity have been measured as a function of temperature for several specimens of Nb_3Sn. The Hall coefficient is positive, with an indicated hole concentration, on a one carrier basis, of about 0.3 holes/atom, as reported in earlier work. A smaller temperature variation was observed (5% over the range 18-300°K for one sample), than is usual for either transition or noble metals. The thermoelectric power of single crystal increases sharply between 18°K and 46°K, and has a weak temperature dependence above 46°K. This temperature presumably marks the tetragonal-cubic transformation in this specimen, and a break in the resistivity is also observed at 46°K. Detailed analysis of the transport data is currently underway.

2. Stress Dependence of the Transition Temperature
(J. P. McEvoy)

An investigation of the effect of a uniaxial compressive stress along the [100] direction on the transition temperature of single crystals Nb_3Sn is nearing completion. The magnitude of the decrease in T_c with increasing stress is found to be a function of the stress applied while

cooling the sample through the cubic-tetragonal transformation at about 50°K. This result, together with the development of marked structure in the T_c (inductance as a function of temperature) curve, can be interpreted as arising from the domain structure in the transformed crystal, the effect of the applied pressure being maximal for those domains which are properly aligned. There is some indication that the application of pressure greater than the 400 atm. maximum to date will permit the development of a single domain, thereby providing a measure of the domain wall energy. On the assumption that the shift in T_c for those domains having the proper orientation is the appropriate result to be compared with theory, we find $\delta T_c/\delta P \sim 10^{-3}$°K/atm., in fair agreement with the theoretical prediction of $\delta T_c/\delta P = 6 \times 10^{-3}$°K/atm. This is about 100 times the effect seen in ordinary superconductors (e.g. Ta), and constitutes an important confirmation of the theory for both the normal and superconducting states.

C. Doping Experiments
(L. J. Vieland and A. W. Wicklund)

Work during this quarter has been concentrated on hydrogen doping of Nb_3Sn. The addition of hydrogen proved to be extremely non-reproducible, and we have been unable to explain this fact, beyond noting that it appears to be a common problem in working with transition metals. We have been able to completely hydride (Nb_3SnH) samples by autoclaving under high H_2 pressure. The material produced is non-superconducting at 4.2°K, and a T_c of 18°K is recoverable by outgassing at 300-500°K.

Neutron diffraction data has been taken in order to locate the position of H atoms in the lattice, and the results will be reported in the next quarter. The peaks associated with H appear to be strongly temperature dependent. Similar results have been reported for Pd, where

the H lattice undergoes a low temperature phase change.

D. In Quest of Hidden Variables
(L. J. Vieland and A. W. Wicklund)

As noted in the conclusions of the appendix, there are insufficiencies in the theory of a serious nature; in particular, the actual forces responsible for triggering the cubic-tetragonal transformation may not yet be known. There is a strong suggestion from susceptibility and specific heat data that antiferromagnetic interactions may be of importance in the β-W superconductors, and we have performed two experiments in an effort to probe possible magnetic interactions.

The first experiment consists simply of looking for magnetic superstructure by neutron diffraction. Although analysis of the data is not complete, there appears to be little difference between the room temperature and liquid neon (27°K) patterns, so that Nb_3Sn does not appear to be magnetically ordered in the tetragonal state.

We have also measured the magnetic field dependence of the elastic constants in the cubic state close to the transformation temperature. Although some refinement of technique is required, it appears that C_{11} at least is field sensitive, decreasing about 0.1% in a field of 20kGauss. This effect is 100 times, and of opposite sign, to the usual field effect in metals, and is also somewhat larger than calculated from the band model for Nb_3Sn. We hope to be able to extend the measurement to higher fields in the near future.

E. Growth of Nb_3Sn from Tin Flux
(J. J. Hanak and D. E. Johnson)

Attempts to grow large single crystals by decreasing the surface area of the nucleating substrate in a Czochralski type apparatus were

unsuccessful because of extensive nucleation at the crucible walls.

Two approaches now under evaluation include possible epitaxial growth on a single crystal niobium seed and the recrystallization of dense polycrystalline Nb_3Sn grown by liquid transport.

APPENDIX

CHARACTERISTIC PARAMETERS OF β-W SUPERCONDUCTORS

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There has been considerable success in understanding the unusual properties of the high temperature cubic phase of the high T_c β-tungsten superconductors[1]. In particular, the temperature dependence of the electrical resistivity, elastic constants $C_{11}(T)$ and $C_{12}(T)$, and the magnetic susceptibility $\chi(T)$ above the lattice transformation temperature T_M have been calculated from a model of the electronic density of states. The model density of states (for both spins) has the form

$$\begin{aligned} N(E) &= N_o, \quad E > 0 \\ &= \alpha N_o, \quad E < 0 \end{aligned} \tag{1}$$

where the quantity α is assumed to be much less than unity. Physically, the model can be interpreted as a high density of states d-band overlapping a wide, low density of states s-band. The d-band is assumed to be nearly empty[2]; the total number of electrons in this band at $T = 0$ is given by $N = (1-\alpha)N_o kT_o$, where kT_o is much less than the width of the band. Furthermore, following Labbe and Friedel[3], we assume that the d-band consists of three independent equal contributions from the orthogonal chains of the β-tungsten lattice. Due to the assumed independence of the sub-bands, under a uniaxial strain ϵ_{ii} directed along the i'th chain ($i = 1,2,3$), only the sub-band associated with that chain is perturbed. In that case, the shift of the edge of the particular sub-band i is given by $\delta E_i = U\epsilon_{ii}$, where U is a deformation potential. By applying the model to the experimental quantities of the cubic state of Nb_3Sn, the parameters of the model were found to be[4] $N_o = 5.6$ states/e.v.-atom, $\alpha = 0.04$, $T_o = 80°K$, and $U = 4.1$ e.v.

The unusual aspects of the model are the sharp drop in the density of states, the very small number of carriers in the d-band, and the response of the d-band to lattice distortion. The sharp drop in the density of states, which greatly facilitates calculations, appears to be necessary in order to accurately reproduce the temperature dependence of experimental quantities in the cubic phase. The independent sub-band approximation has been shown to give good results for small strains in the cubic state[1]. The present paper applies the band model to the tetragonal state ($T < T_M$) using the parameters obtained from the cubic state data. We calculate the magnetic susceptibility, specific heat, elastic constants, and the tetragonal distortion, and compare with experimental data. The agreement between theory and experiment is, in some cases, excellent. However, certain discrepancies suggest that the transformed state can not be described solely by a tetragonal strain imposed on the cubic state model.

In order to calculate the experimental quantities in the tetragonal state, we make use of the expression for the free energy of the system in the presence of a magnetic field H, tetragonal strain ϵ, and uniaxial strains[5] η. Neglecting the small contribution of the s-electrons, the free energy is given by

$$F(T,E_F,\epsilon,\eta,H) = NE_F + \tfrac{1}{2}\sum_{\ell=\pm 1}\sum_{m=\pm 1}(m+3)\,g(\tfrac{1}{4}[3m-1]U\epsilon + U\eta + \ell\mu_B H, T, E_F) + (3/4)(A_{11}-A_{12})\epsilon^2 + (3/2)(A_{11}+2A_{12})\eta^2 - \tfrac{1}{2}\chi_{orb}H^2, \quad (2)$$

where

$$g(X,T,E_F) = -(N_o/6\beta)\int_X^\infty \ln\{1 + \exp - \beta(E-E_F)\}dE. \quad (3)$$

In Eqs. (2) and (3), A_{11} and A_{12} are temperature independent lattice contributions to C_{11} and C_{12}, respectively[6], χ_{orb} is the temperature independent orbital contribution[1] to the susceptibility,

E_F is the Fermi energy, N is the total number of d-band electrons, and $\beta=(k_B T)^{-1}$. The position of the Fermi level is established by the condition $\partial F/\partial E_F=0$.

The value of the tetragonal deformation $\epsilon_o(T)$ is found from the condition for equilibrium (in the following, all derivatives are evaluated at $\eta = H = 0$ and $\epsilon = \epsilon_o(T)$):

$$\partial F/\partial \epsilon = 0. \tag{4}$$

Below the lattice transformation temperature T_M there are two solutions for ϵ_o which correspond to free energy minima; that for which $\epsilon_o > 0$ has the lower free energy and corresponds to the sign of the transformation for[7] Nb_3Sn. The transformation temperature T_M is given in terms of the parameters of the theory through the approximate relation

$$T_M \approx -T_o\{\ln[1-3(A_{11}-A_{12})/N_o U^2]\}^{-1}. \tag{5}$$

In Fig. (1) is shown the theoretical curve of ϵ_o as a function of T/T_M. The experimental values of Mailfert et. al.[7] are given in the figure. The agreement between theory and experiment is good over most of the temperature range. It is noteworthy that the value of ϵ_o at $T = 0°K$ has not been fitted to the data; it is based on parameters of the model extracted from cubic state data. At the transformation temperature, the theory predicts a first order transformation with a large jump in ϵ_o. The temperature resolution in the x-ray measurements is not sufficient to detect a discontinuity in ϵ_o, but no hysteresis was observed[7]. Furthermore, the x-ray data[7] indicates that $T_M = 43°K$, whereas the elastic constant data [Eq. (5)] predicts $T_M \approx 50°K$. At present, we do not know the origin of this difference.

The elastic constants in the tetragonal state can be derived from the free energy function (2) according to the relations

$$\frac{3}{2}\,(C_{11}(T)-C_{12}(T)) = \partial^2 F/\partial\epsilon^2 \qquad (6a)$$

$$3(C_{11}(T)+2C_{12}(T)) = \partial^2 F/\partial\eta^2. \qquad (6b)$$

The solution to Eqs. (6) indicates that the elastic constants return to the lattice values at low temperatures. Physically, this result comes about because of the fact that the stable state of the system at low temperatures is one in which all electrons are in one sub-band. Thus, there is no term in the electronic contribution to the free energy which is quadratic in ϵ or η. The predicted return of the elastic constants to the lattice values been observed in Nb_3Sn by Rehwald[8], and for completeness, the author's results are reproduced in Fig. (2).

The electronic specific heat at constant volume in the tetragonal state is obtained from the equation

$$C_V(T) = -T\partial^2 F/\partial T^2. \qquad (7)$$

In Fig. (2) is shown the calculated curve of $C_V(T)$ obtained from Eqs. (2)-(4) and (7). Since the major contribution to the specific heat comes from the lattice modes, it is necessary to fit the curve for the cubic state near T_M by choosing an appropriate Debye temperature. Otherwise, there are no adjustable parameters. It is gratifying that the specific heat jump at T_M, and the magnitude of the energy associated with the rapidly changing strain just below T_M are in excellent agreement with theory. However, theory predicts a distinctly first order transition at T_M, with a latent heat of 2 Joules/g-atom, which is not observed. The failure to observe a latent heat cannot be attributed to a smearing of the transition which would distribute the large latent heat over the region below T_M.

The paramagnetic susceptibility is obtained from Eqs. (2) and (3) according to the relation

$$\chi(T) = -\partial^2 F/\partial H^2. \tag{8}$$

The result is

$$\chi(T) = \tfrac{1}{3}\bar{N}_o \mu_B^2 \{f(-U\epsilon_o) + 2f(\tfrac{1}{2}U\epsilon_o)\} + \chi_{orb}, \tag{9}$$

where f(E) is the Fermi function. In Eq. (9), the quantity $\bar{N}_o$ represents a weakly temperature dependent density of states which has been renormalized in order to take into account many-body effects[9]. Analysis of cubic state data[1] shows that $\bar{N}_o$ = 3.3 states/e.v. atom. Fig. (4) shows the normalized susceptibility as a function of temperature for a sample which was similar to that shown in Figs. (1) - (3). The theoretical curves are for the cubic state $\epsilon_o = 0$ and the tetragonal state [Eq. (4)]. The unusual low temperature maximum in the susceptibility follows from the theory and arises because as the temperature is lowered all electrons spill into one sub-band with effective density of states $\bar{N}_o/3$. However, the observed decrease in the susceptibility is only about two-thirds of the expected drop. Also, the susceptibility of a crystal which shows the elastic constant[10] $(C_{11}-C_{12})$ going to zero at 32°K is roughly temperature independent below approximately 60°K. Thus, the susceptibility of this crystal departs from the cubic state theory at temperatures well above the predicted T_M.

We have seen that using cubic state parameters and a simple band structure model, we are able to obtain good agreement with the overall behavior of the tetragonal state properties. In some cases, such as the value of the tetragonal deformation and the magnitude of the elastic constants, striking quantitative agreement is obtained. In spite of this success, it is felt that the discrepancies that do exist are fundamental in nature. In particular, the absence of a latent heat, the

discrepancy between the values of T_M determined from various experiments, and the lack of quantitative agreement for the susceptibility suggest that the theory is incomplete. Moreover, an analysis of the observed[11] temperature variation of $[C_{11}(T)-C_{12}(T)]$ for V_3Si shows excellent agreement with Eq. (6a) using V_3Si parameters and indicates, in contrast to the results of x-ray experiments[12], that no tetragonal transformation should occur in this material. It is believed that the mechanism which triggers the tetragonal transformation has not been completely identified.

References and Footnotes

1. R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Letters 19, 840 (1967).
2. We could, of course, consider a nearly filled d-band.
3. J. Labbe and J. Friedel, J. Phys. Radium 27, 153, 303 (1966) (2 papers).
4. These values of T_o and U are slightly different than those given in Reference 1, owing to further experimentation and more complete characterization of specimens. The value of N_o has been obtained from specific heat measurements (L. J. Vieland and A. W. Wicklund, Phys. Rev. 166, 424 (1968)).
5. In conventional notation, the individual strain components are $\epsilon_{11} = (\eta-\epsilon)$ and $\epsilon_{22} = \epsilon_{33} = (\eta + \frac{1}{2}\epsilon)$. We are ignoring the small differences between the elastic constants C_{11}, C_{22}, and C_{33} in the tetragonal state.
6. We have neglected all higher order lattice contributions, a detailed analysis shows this to be a valid approximation in Nb_3Sn over the temperature range of interest.
7. R. Mailfert, B. W. Batterman, and J. J. Hanak, Phys. Letters 24A, 315 (1967).

8. W. Rehwald, Phys. Letters (in press).

9. A. M. Clogston, Phys. Rev. 136, A8 (1964).

10. K. R. Keller and J. J. Hanak, Phys. Rev. 154, 628 (1967).

11. L. R. Testardi and T. B. Bateman, Phys. Rev. 154, 402 (1967).

12. B. W. Batterman and C. S. Barrett, Phys. Rev. Letters 13, 390 (1964); Phys. Rev. 145, 296 (1966).

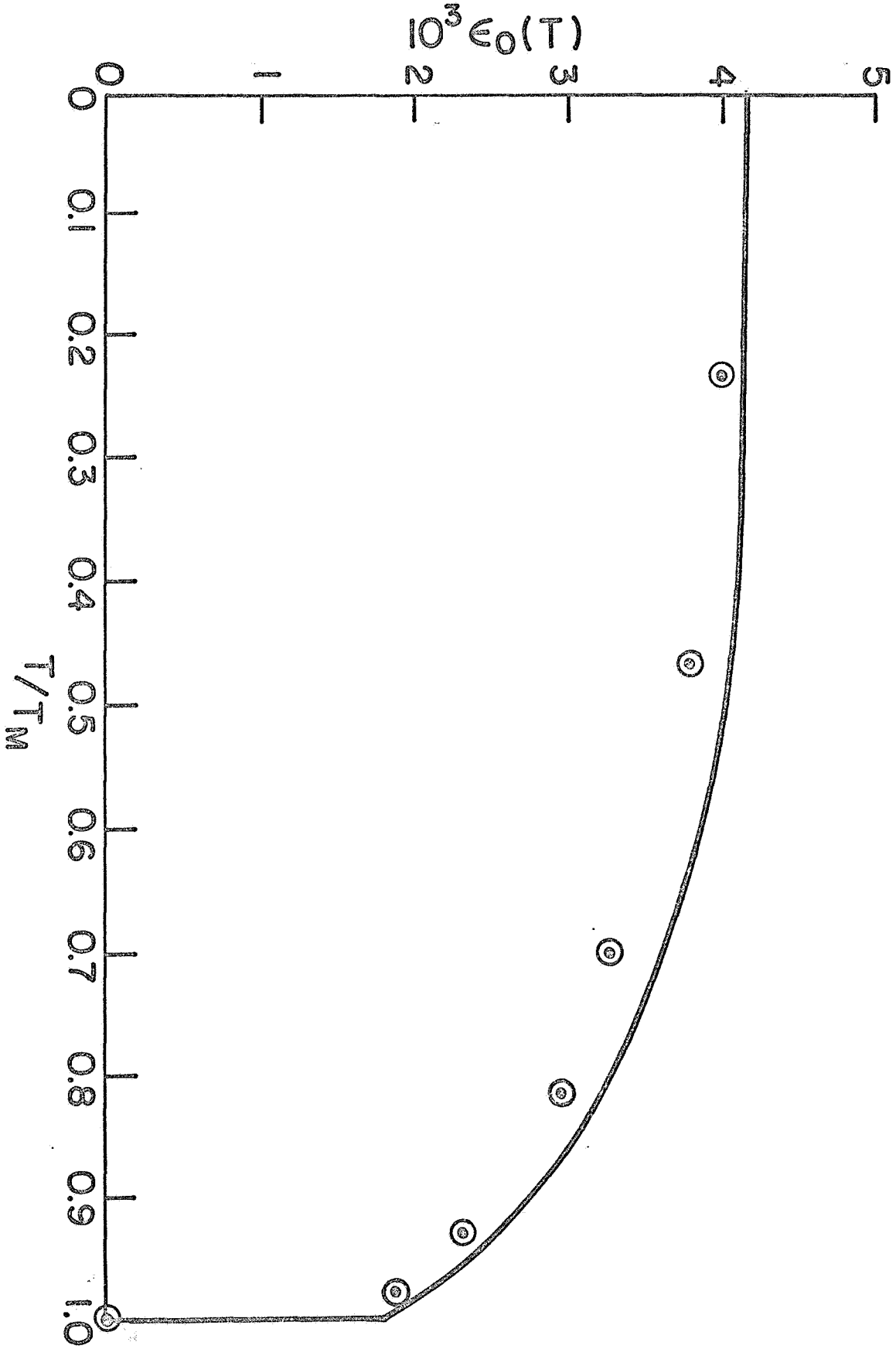


Figure 1

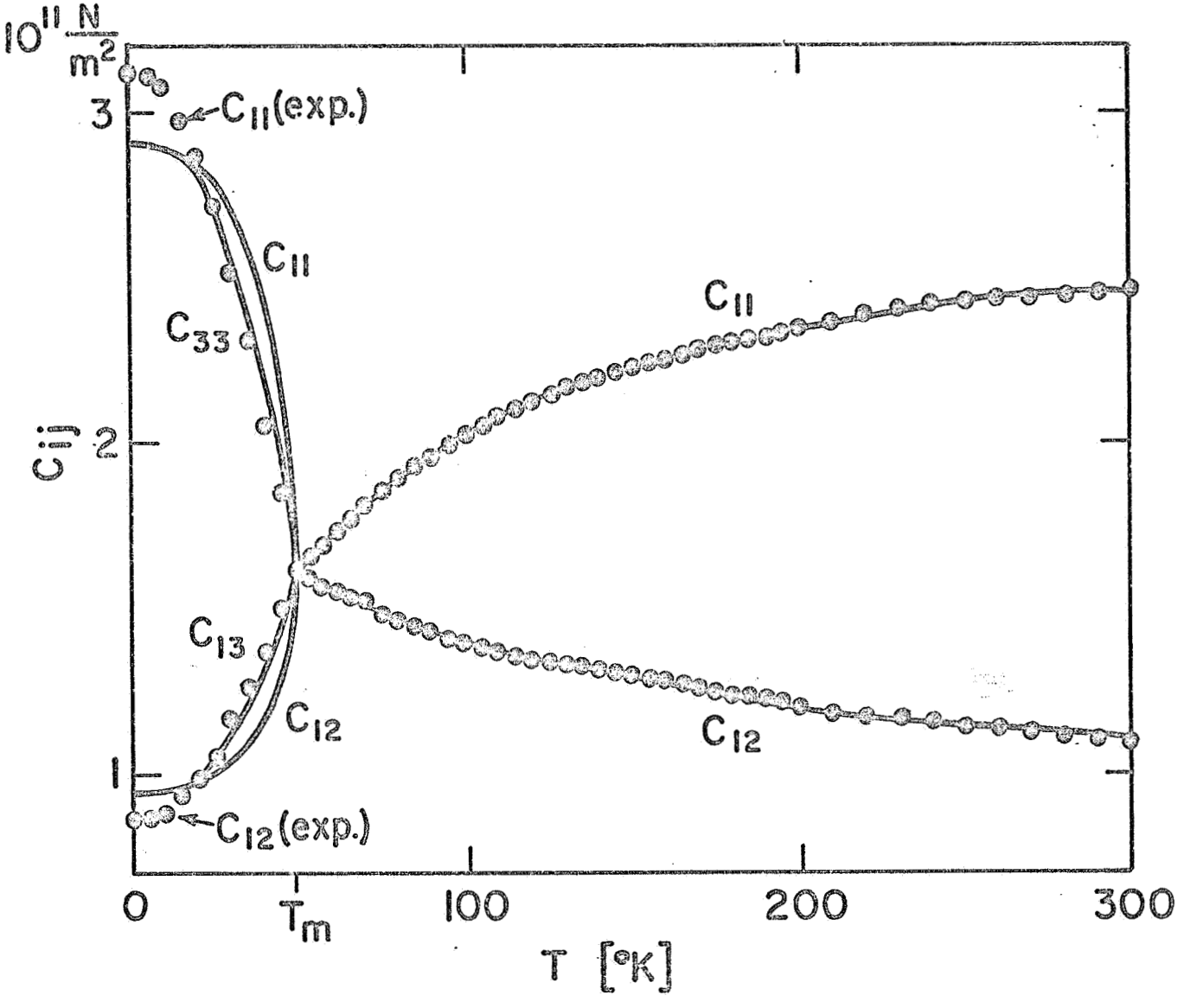

$10^{11}\frac{N}{m^2}$
3
2
1
C_{ij}
C_{11}(exp.)
C_{11}
C_{33}
C_{13}
C_{12}
C_{12}(exp.)
C_{11}
C_{12}
0
T_m
100
200
300
T [°K]

Figure 2

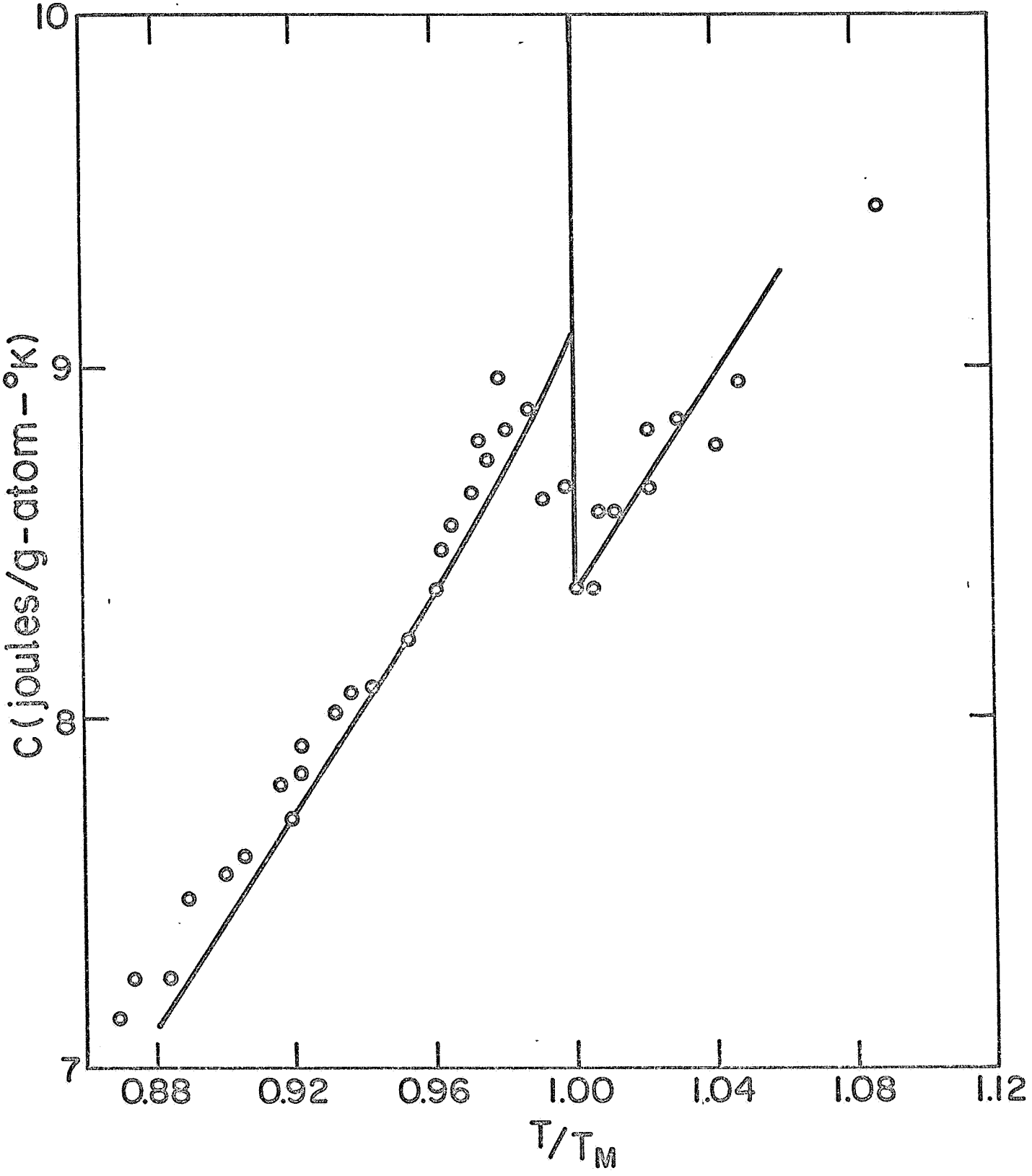
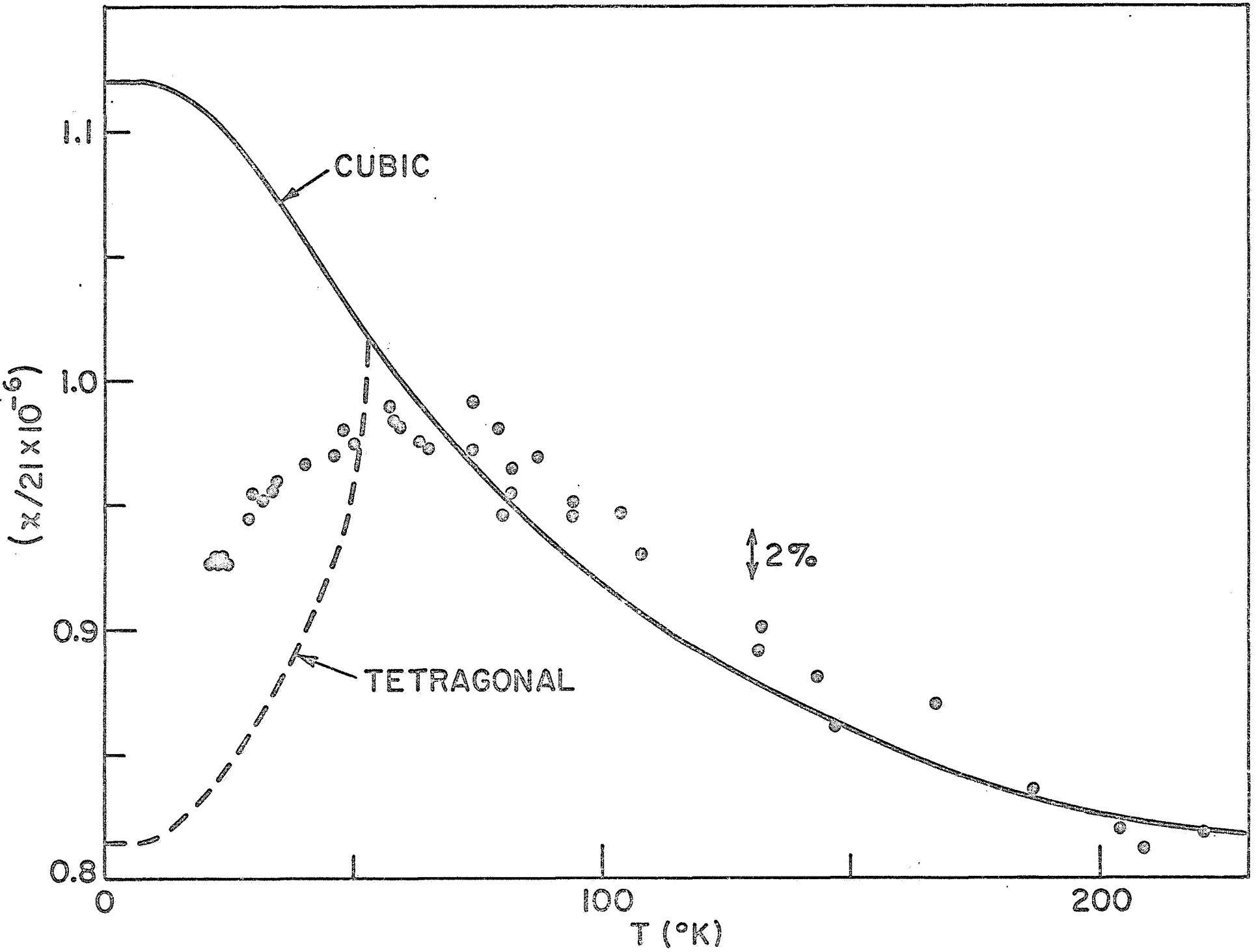


Figure 3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(χ/21×10⁻⁶)
CUBIC
TETRAGONAL
2%
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T (°K)