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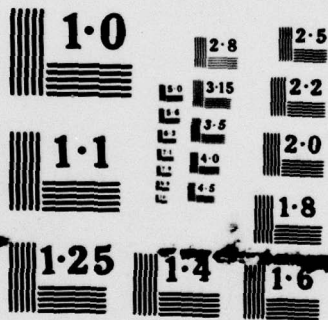
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Technical Report Number 8

PREPARATION AND PROPERTIES OF A COPPER NIOBIUM OXYFLUORIDE

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October 1, 1979

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ABSTRACT

A fluorinated phase of copper niobium oxide with the formula $\text{CuNb}_2\text{O}_{5.3}\text{F}_{0.7}$ has been synthesized. The oxyfluoride displays orthorhombic symmetry with $a = 9.665(5)$, $b = 10.40(3)$, and $c = 7.85(3)\text{\AA}$. Magnetic susceptibility data indicates a Curie Weiss behavior consistent with the quantity of $\text{Cu}^{2+}(\text{d}^9)$ present. The measured room temperature resistivity is $0.5\ \Omega\text{-cm}$ and the electronic activation energy of $0.06\ \text{eV}$ indicates some electron delocalization.

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INTRODUCTION

The chemistry of transition metal oxyfluorides has aroused interest in recent years. In view of the fact the oxygen and fluorine have similar ionic radii¹ the possibility of fluoride incorporation into these systems exists without creation of large structural changes. Such substitutions have been shown to occur in the formation of spinel,² magnetoplumbite, garnet,³ perovskite⁴ and rutile⁵ oxyfluorides.

Another group of compounds are formed when niobium pentoxide reacts with divalent and trivalent ions and have structures related to rutile. In nature the mineral columbite, iron(II) or manganese(II) niobate, occurs with a unique structure. The objective of this work was to prepare and characterize a copper niobium oxyfluoride crystallizing with the columbite structure. The preparation was achieved by a new fluorination technique.

EXPERIMENTAL

Material Preparation. The starting material, CuNb_2O_6 , was prepared by solid state reaction between CuO , which was synthesized by successive oxidation of metallic copper (Matthey S-50250A) under oxygen atmosphere, and Nb_2O_5 (KBI 270-A). The proper molar ratio of the two were mixed in a high speed mill and pressed into small pellets. The pellets were then placed on a platinum disc and subjected to heat at 1000°C in a tube furnace for 24 hours under a continuous flow of oxygen. The material was obtained as a dark green powder.

Fluorination. The fluorination apparatus consisted of two nickel tubes placed in two separate tube furnaces. HF was generated by means of the thermal decomposition of potassium bifluoride (ROC/RIC 95%), a sufficient quantity of which was placed in a nickel boat and positioned in one of the nickel tubes. The sample was then placed on platinum in a second nickel boat and positioned in the second nickel tube. The two tubes were connected together and also to the carrier gas tanks in such a fashion that as the HF was generated, it was carried by a gas stream which first passed through a flowmeter and a phosphorous pentoxide drying tube, then over the sample and finally exited into a trap containing a 5% solution of sodium hydroxide.

The fluorination reactions were carried out on pressed pellets of copper niobate using 15% H_2/Ar as the carrier gas which also served as reducing agent. The apparatus described above allowed working temperatures of up to 800°C . The fluorinations were usually allowed to take place for four hours. At 800°C

dark brown, well sintered discs were produced which were then subjected to chemical and physical as well as x-ray measurements.

X-ray Analysis. The x-ray data were collected on a powder sample using the Guinier Camera with Copper radiation ($\lambda = 1.5405$) and Silicon ($a = 5.43062\text{\AA}$) as an internal standard.

Chemical Analysis. The fluoride content of the sample was leached out by means of sodium hydroxide fusion in a platinum boat. The process was carried out in a closed system to ensure that no fluoride escaped. The fluoride ion concentration was then determined using a fluorine sensitive electrode (Orion 94-09) and a Leeds & Northrup 7415 pH meter.

Density Measurements. Density measurements were made using a hydrostatic technique based on Archimedes Principle.⁶ The liquid medium was perfluoro 1-methyl decaline (Pierce Chemical Company) and the balance used was a Mettler H-54. The liquid medium was standardized using a high purity silicon standard (Atomergic Chem. Metals), $\rho = 2.328 \text{ g/cm}^3$.

Magnetic Measurements. The magnetic susceptibilities were measured using a Faraday balance⁷ over a range of liquid nitrogen to room temperature and a field strength of 10.4 KOe. Honda-Owen plots were also made in order to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism.⁸

Electrical Measurements. Electrical measurements were made using the standard van der Pauw technique.⁹ Indium leads were placed on the sample ultrasonically and then soldered to the terminals of high resistivity epoxy cement blocks.

RESULTS AND DISCUSSION

Fluorination of CuNb_2O_6 resulted in the formation of an oxyfluoride with a density of $5.18 \pm 0.1 \text{ g/cm}^3$. The x-ray diffraction data for this compound is given in Table I. The peaks were tentatively indexed on the basis of an orthorhombic unit cell with the cell parameters $a = 9.665(5)$, $b = 10.40(3)$ and $c = 7.85(3)$. However, the relative intensities and positions of a few of these peaks lead to some reservation with respect to the assignment made.

The results of the chemical analysis indicated the presence of 0.7 mole of fluorine per mole of the oxyfluoride. Moreover, the magnetic data indicates that the material is paramagnetic containing no ferromagnetic impurities as determined by the field independent Honda-Owen plot. Fig. 1 shows the plot of χ^{-1} vs temperature for copper niobate, CuNb_2O_6 , with a μ_{eff} of $2.08 \mu_B$. This value is within the expected range of magnetic moments of $1.8 - 2.2 \mu_B$ ⁸ observed for $\text{Cu}^{2+}(\text{d}^9)$ systems.

Fig. 2 affords the plot of χ^{-1} vs temperature for the oxyfluoride system with a spin only moment of $0.68 \mu_B$. This value corresponds to the presence of 0.22 mole of Cu^{2+} in the fluorinated sample with the remainder being Cu^{1+} . This is in reasonable agreement with the chemical analysis.

The resistivity measurements are given in Fig. 3. The material shows a room temperature resistivity of 0.5 ohm-cm and a low activation energy of 0.06 eV . The failure to obtain any Hall voltage indicates a low mobility and hence there must be a large number of carriers present.

Attempts were made to prepare copper niobium oxyfluorides with varying amounts of fluorine. The two procedures used were first the fluorination of CuNb_2O_6 using H_2/Ar as the carrier gas, and second, the use of pure hydrogen as the carrier gas. The former method gave essentially identical products down to 600°C ; the latter tended to result in the formation of decomposition products.

In view of these observations it can be concluded that the limit of fluorination was reached and that the maximum amount of fluorination achieved corresponded to the compound $\text{CuNb}_2\text{O}_{5.3}\text{F}_{0.7}$. Moreover, the high electrical conductivity of this compound may be attributed to the presence of both $\text{Cu}^{1+}(\text{d}^{10})$ and $\text{Cu}^{2+}(\text{d}^9)$ with some delocalization of the 3d electrons. This is of interest because the tendency of fluorides to localize such 3d states.

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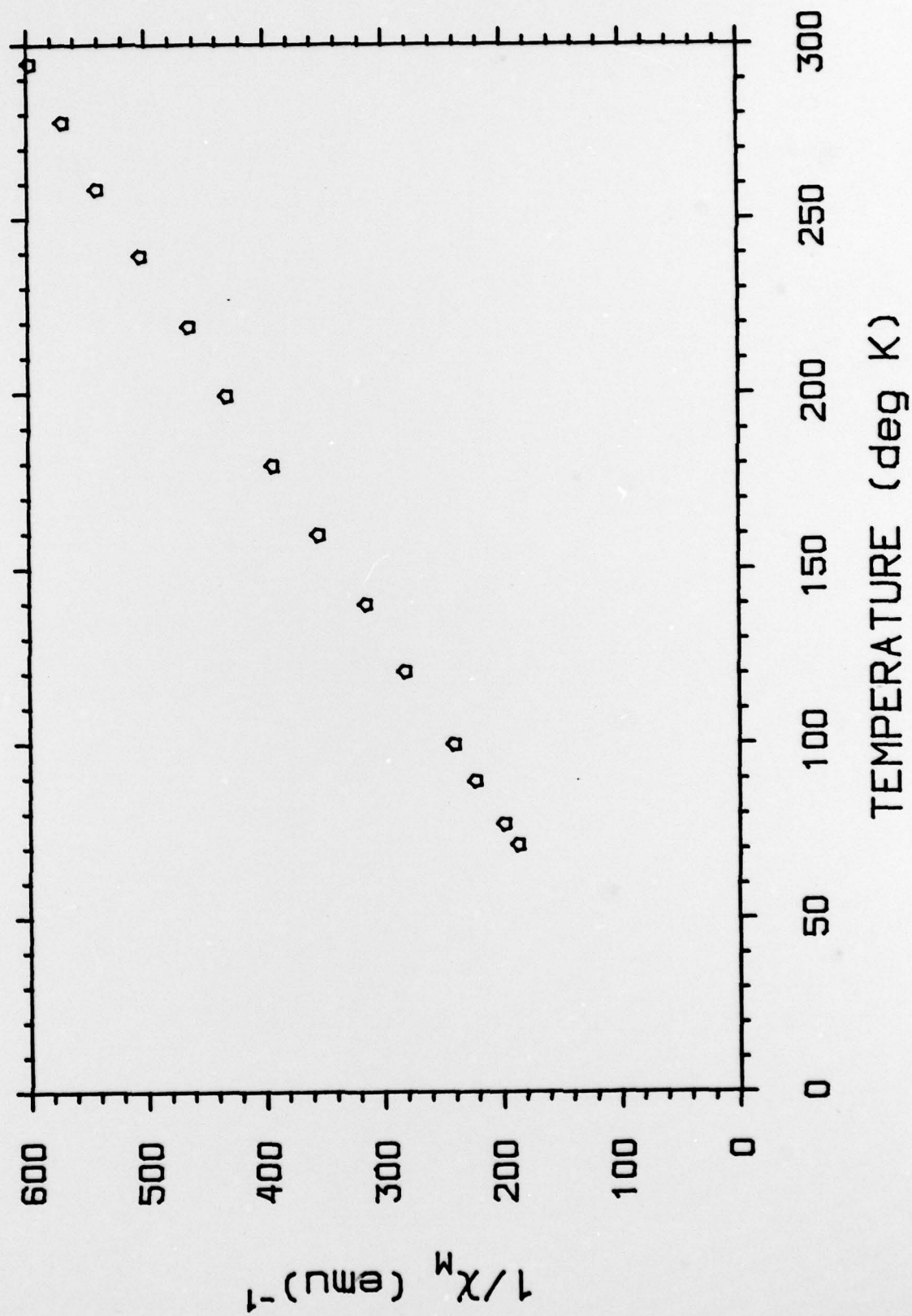
TABLE I
X-RAY DATA ON $\text{CuNb}_2\text{O}_{5.3}\text{F}_{0.7}$

Intensity	$d_{\text{obs.}}$	$d_{\text{calc.}}$	hkl
6	5.209	5.198	020
1	4.869	4.833	200
90	3.932	3.923	002
3	3.467	3.465	030
100	3.140	3.131	022
50	3.079	3.077	310
1	2.871	2.865	311
3	2.727	2.838	320
3	2.599	2.599	040
53	2.451	2.453	113
26	2.422	2.421	312
5	2.411	2.416	400
2	2.354	2.353	410
2	2.313	2.309	401
2	2.167	2.167	042
5	2.114	2.114	142
80	2.088	2.088	033
3	2.032	2.032	150
8	2.008	2.009	051
3	1.975	1.977	242
30	1.960	1.962	004
5	1.860	1.856	251
5	1.843	1.844	043
20	1.828	1.820	204
31	1.807	1.805	152
28	1.789	1.790	214
2	1.764	1.765	521
2	1.733	1.732	060
2	1.706	1.705	160
30	1.665	1.666	161
17	1.655	1.654	314

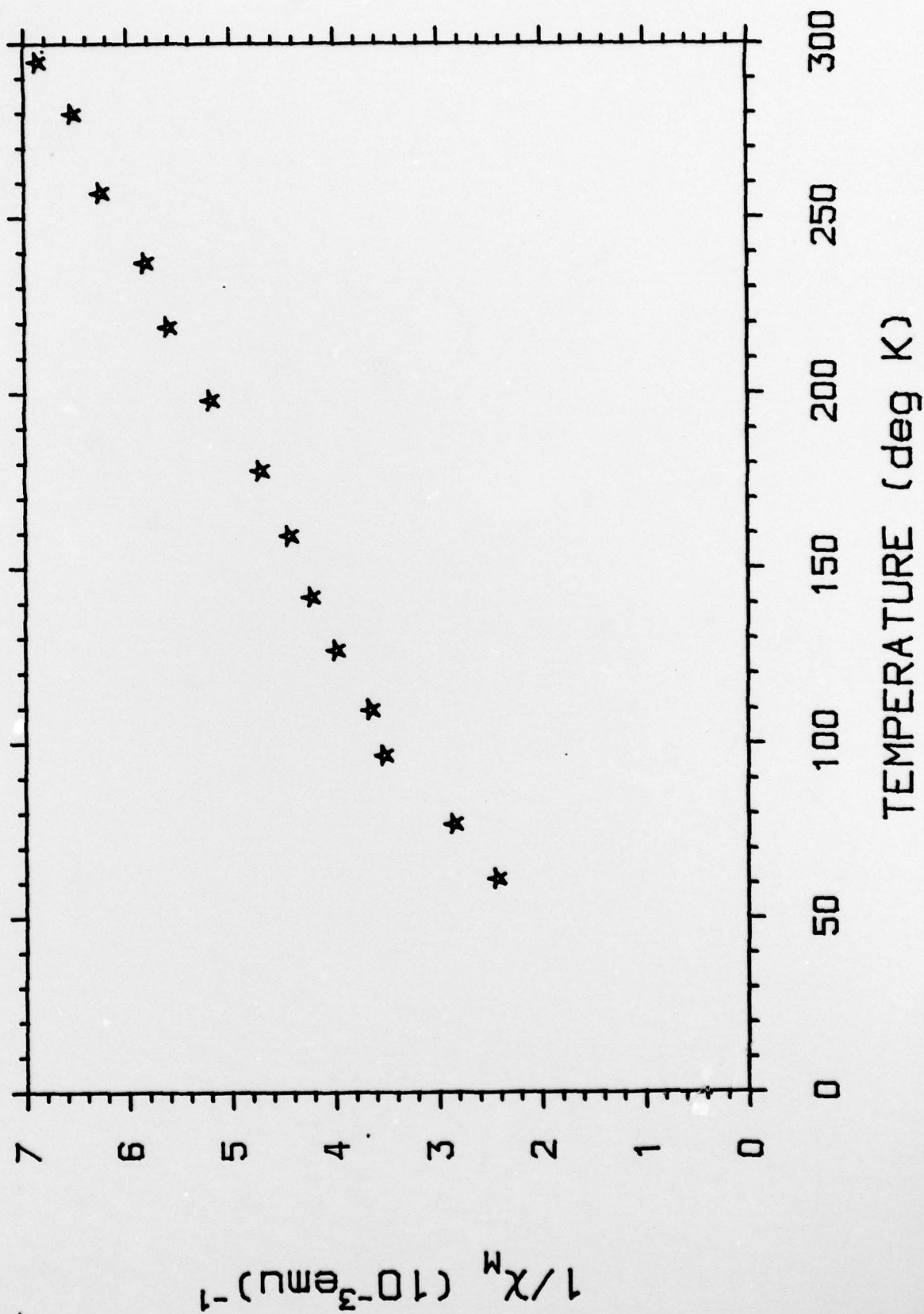
FIGURE CAPTIONS

- Fig. 1 - Thermal variation of the molar magnetic susceptibility of copper niobate. The slope corresponds to a μ_{eff} of $2.08 \mu_B$.
- Fig. 2 - Thermal variation of the molar magnetic susceptibility of fluorinated copper niobate. The slope corresponds to a μ_{eff} of $0.68 \mu_B$.
- Fig. 3 - Thermal variation of the resistivity of fluorinated copper niobate. The slope corresponds to an activation energy of 0.06 eV.

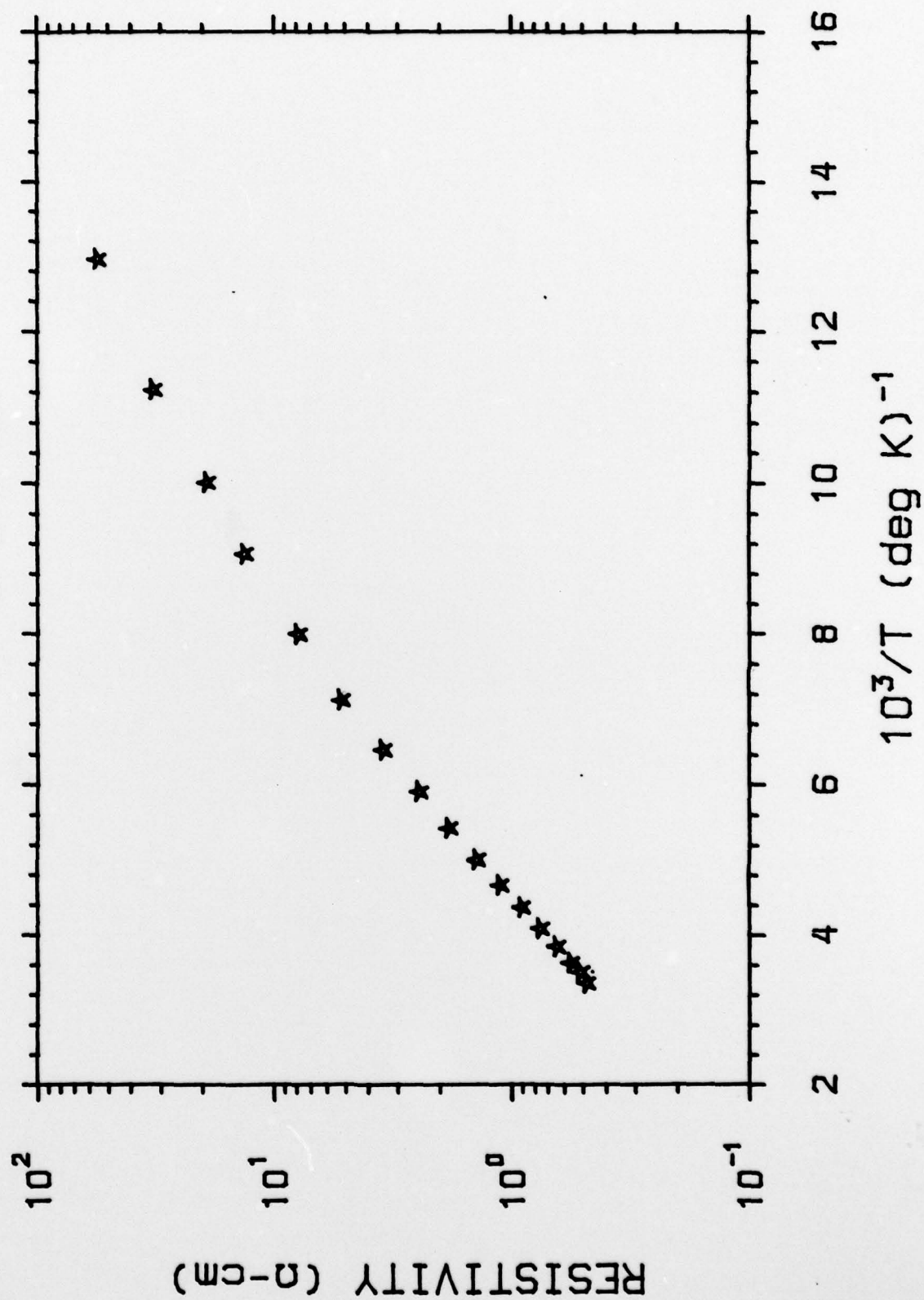
CuNb_2O_6



$\text{CuNb}_2\text{O}_{5.3}\text{F}_{0.7}$



$\text{CuNb}_2\text{O}_{5.3}\text{F}_{0.7}$



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