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Solid-State Studies of Potassium Molybdenum Bronzes[1]

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Potassium molybdenum bronzes, K_xMoO_3, have been prepared by electrolytic reduction of molten K_2MoO_4–MoO_3 (1:3.15 molar ratio) mixtures. Single-crystal electrical conductivity studies confirm that the blue bronze $K_{0.30}MoO_3$ is metallic above 180°K whereas the red bronze $K_{0.33}MoO_3$ is practically an insulator at room temperature. Magnetic susceptibilities, measured by the Gouy method over the range 1.5–300°K, are small and nearly temperature independent; at 300°K, residual χ per mole of K_xMoO_3 is 70×10^{-6} cgs unit for the red bronze and 20×10^{-6} cgs unit for the blue. Hall voltage and thermoelectric data have been measured on the blue bronze in the range 100–300°K. Results above 180°K indicate a high concentration of p-type carriers; below 180°K, a low concentration of n-type carriers. The above differences in behavior are attributed to differences in molecular orbital population and electron delocalization over the Mo_6O_{18} and $Mo_{10}O_{30}$ clusters that make up the red and blue bronzes, respectively. The change from n to p character in the blue bronze is explained by a two-carrier model.

Introduction

Wold, Kunnmann, Arnott, and Ferretti[2] have reported a remarkable difference in electrical conductivity between the red and blue potassium molybdenum bronzes. The red bronze, to which they ascribe the formula $K_{0.26}Mo_{1.01}O_3$, showed typical semiconduction behavior with a positive temperature dependency; the blue bronze, $K_{0.28}Mo_{1.02}O_3$, had a much lower resistivity with an apparent transition from semiconductor to metallic behavior above −100°. The structures of the red and blue bronzes as worked out by Stephenson and Wadsley[3] and Graham and Wadsley,[4] respectively, are somewhat different from each other but have the common feature of a layerlike arrangement of clusters of edge-sharing MoO_6 octahedra. As part of a general program in this laboratory to study the electric and magnetic properties of nonstoichiometric transition metal compounds, it was desirable to define the solid-state parameters (carrier sign, density, and mobility) of these molybdenum bronzes.

Experimental Section

Preparation of Materials.—Following the method of Wold, *et al.*,[2] single crystals were prepared by electrolysis of molten mixtures of MoO_3 and K_2MoO_4 in a very carefully controlled range of temperature and composition. With 3.15:1 molar ratio of MoO_3:K_2MoO_4 in a two-compartment porcelain electrolytic cell, red crystals were formed at 570° and blue crystals at 550°. The platinum spiral cathode was in the outer, lower compartment, and the platinum rod anode, in the inner, upper compartment. Temperature was controlled from a sensing thermocouple fitted into a Vycor well in the upper compartment. Current density was approximately 10 ma/cm^2. (The favoring of red bronze at the higher temperature is probably an entropy effect, associated with favoring smaller polymolybdate clusters—hence, greater entropy—at higher temperatures.) Good platelike crystals, averaging 5 × 2 × 1 mm in dimensions, were picked out from the solidified, quenched melt. Microscopic examination of the crystals used for the conductivity and Hall voltage studies failed to disclose any admixture of red phase in the blue crystals.

Analysis of Materials.—Starting materials were Climax Molybdenum reagent grade MoO_3 and Shattuck Chemical reagent grade K_2MoO_4. Spectroscopic analysis of products indicated no metallic elements other than K and Mo at significantly greater than detection limits. Direct analysis for K was by flame photometry; for Mo, by thiocyanate colorimetry. Oxygen was determined by difference. Results corresponded to $K_{0.34}MoO_3$ for the red bronze and $K_{0.29}MoO_3$ for the blue. Potassium content was confirmed by a sensitive method based on measurement of total reducing power. For this, samples of bronze were dissolved in K_2CO_3 solution containing $Ag(NCS)_4^{3-}$, and the precipitated Ag, after being dissolved in HNO_3, was determined by the Volhard method. Precision on the K analysis was about 10% by the flame photometer method and 1% by the reducing method. Precision on the Mo analysis was 2%.

Electrical Conductivity.—Measurements were by the potential-probe method using current-feed probes of copper at the ends of the crystal and copper or constantan sensing probes on a side of the crystal. Crystal dimensions and probe spacing were measured with a stage-micrometer-calibrated microscope. Crystals of red bronze gave room-temperature resistivities of the order of 10^4 ohm-cm; crystals of blue bronze gave room-temperature resistivities of the order of 10^{-4} ohm-cm. Representative changes with temperature for two crystals of the blue are summarized in Figure 1. Values for crystal 2 are believed to be the more accurate because of better signal-to-noise ratio. Constancy of the IR/I ratio over a range of currents indicated that behavior was strictly ohmic.

Hall Voltage.—The Hall voltage generated in a constant magnetic field was measured using ac techniques with lock-in phase sensitive detection. Direct proportionality to the magnetic field and reversal of sign on field reversal confirmed that a true Hall voltage was being observed. In the absence of a magnetic field, a virtual equipotential plane was established across the crystal by attaching one of the Hall probes to the center tap of a misalignment potentiometer connected in parallel across two indium probes melted against one side of the crystal. Details of the Hall voltage circuitry will be published elsewhere.[5] Results of Hall voltage measurement on a representative blue bronze crystal are shown in Table I, the most striking feature of which is the shift from n-type behavior at low temperatures to p-type behavior at room temperature.

Magnetic Susceptibility.—The magnetic susceptibility of powder samples was measured over the range 1.5–300°K, using the Gouy balance and cryogenic system previously described.[6]

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[1] This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 796-65 and was supported in part by the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

[2] A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.*, **3**, 545 (1964).

[3] N. C. Stephenson and A. D. Wadsley, *Acta Cryst.*, **18**, 241 (1965).

[4] J. Graham and A. D. Wadsley, *ibid.*, **20**, 93 (1966).

[5] J. Perlstein, Ph.D. Thesis, Cornell University.

[6] M. J. Sienko and J. Sohn, *J. Chem. Phys.*, **44**, 1369 (1966).

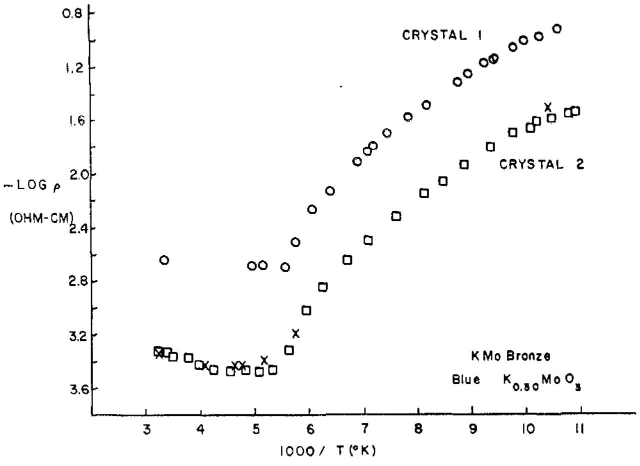

Figure 1.—Resistivity *vs.* reciprocal temperature for two crystals of blue potassium molybdenum bronze. Squares and X's represent heating and cooling cycles, respectively; circles are for cooling.

TABLE I

HALL DATA FOR BLUE KMo BRONZE

Temp, °K	Hall constant, R_H, cc/coulomb	Carrier density,[a] n or p, cc^{-1}	Conductivity, σ, ohm^{-1} cm^{-1}	Hall mobility, $\mu_H = \|R_H\|\sigma$, cm^2 v^{-1} sec^{-1}
74	−3.5	1.8×10^{18} n	7.12	25
92	-7.7×10^{-1}	8.1×10^{18} n	1.71×10^{1}	13
102	-2.9×10^{-1}	2.15×10^{19} n	3.28×10^{1}	9.6
121	-5.3×10^{-2}	1.2×10^{20} n	1.04×10^{2}	5.5
131	-2.5×10^{-2}	2.5×10^{20} n	1.73×10^{2}	4.4
135	-1.6×10^{-2}	4.0×10^{20} n	2.06×10^{2}	3.2
146	-1.2×10^{-3}	5.0×10^{21} n	2.88×10^{2}	0.36
164[b]	$+1.5 \times 10^{-3}$	4×10^{21} p	8.5×10^{2}	~1
292	$+1.5 \times 10^{-3}$	4.2×10^{21} p	2.52×10^{3}	3.8

[a] Assuming one kind of carrier only at each temperature. Carrier density is calculated from the reciprocal of the Hall constant. [b] The values at this temperature are uncertain. A range was observed which extended to $R_H = +1.5 \times 10^{-4}$ and p density = 4×10^{22} corresponding to $\mu_H = 0.1$.

Samples were contained in precision-bore quartz tubes of 4-mm diameter to a height of 12–20 cm. Forces due to imposition of the magnetic field were measured with a Mettler H-6 microbalance over a field range from 0 to 5800 gauss. Susceptibilities were determined by extrapolation to zero reciprocal field; the field dependence of the red bronze was considerably greater than that for the blue. Slopes of χ *vs.* $1/H$ were the same at all temperatures. Figure 2 shows the extrapolated paramagnetic susceptibility per mole of K_xMoO_3 as a function of temperature after subtraction of the diamagnetic susceptibility[7] of K^+ and the observed susceptibility of MoO_3.[8] The temperature dependence of the blue bronze may be only apparent because of the extremely small values involved. The change with temperature is about equal to the diamagnetic correction.

Thermoelectric Power.—The Seebeck coefficient was measured over a range of temperature by determining the voltage between the copper legs of two copper–constantan thermocouples fastened at the ends of a single crystal heated at one end and tied to a heat sink at the other. Indium amalgam was used at the thermocouple–crystal junction to ensure thermal contact. The course of the Seebeck coefficient as a function of temperature is shown in Figure 3. Values shown are uncorrected for the small contribution of copper to the emf.

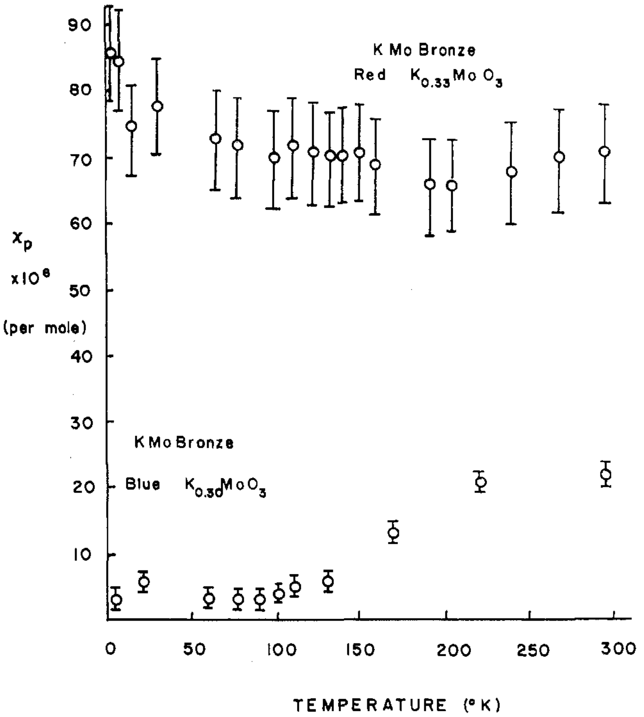

Figure 2.—Net paramagnetic susceptibility per mole of K_xMoO_3 *vs.* temperature.

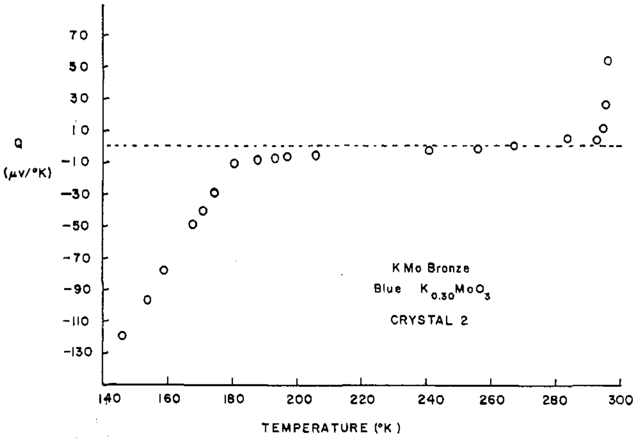

Figure 3.—Seebeck coefficient, voltage difference per degree of temperature difference between the hot and cold ends of crystal, as a function of temperature. The sign of Q refers to the sign of the cold junction relative to copper.

Discussion

In analogy with the tungsten and vanadium bronzes, the simplest model for a molybdenum bronze would be that of an insulating host matrix MoO_3 in which interstitial K atoms have been inserted to provide electrons. In both tungsten and vanadium bronzes, the alkali insertion atom appears to be strictly ionic so it is reasonable to assume in K_xMoO_3 that the K is also in the state of a K^+ ion, having transferred its valence electron to the MoO_3 network. In the case of the M_xWO_3 (M = alkali metal) tungsten bronzes, which are metallic, there is no activation energy for electron transport, so the energy of any donor center formed by electron transfer from M to W^{6+} must lie in or above the conduction band or the donor centers must

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(7) P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, p 78.

(8) J. Baudet, *J. Chim. Phys.*, **58**, 853 (1961).

overlap to form a donor-center (impurity) band. In the case of the $M_xV_2O_5$ vanadium bronzes, which are semiconducting, there is an activation energy for electron transport, and the donor centers must be localized.[6] The molybdenum bronzes K_xMoO_3 appear to be intermediate between the tungsten bronzes and the vanadium bronzes. The blue bronze in particular shows the low susceptibility of the former and, at least below 180°K, the semiconductive character of the latter.

For the quantitative explanation of the K_xMoO_3 solid-state properties, an uncertainty exists in the chemical characterization of the compounds. Wold, *et al.*,[2] on the basis of flame photometric analyses, report the blue bronze to be $K_{0.28}MoO_3$ and the red, $K_{0.26}MoO_3$. In terms of the model described above, where K transfers its valence electron to localized or delocalized states on the MoO_3 network, the net reducing ability of the K_xMoO_3 material should be equally well described by equivalent content of K, Mo^{V}, or Mo^{IV}. Wold, *et al.*,[2] report in their paper analytically determined Mo^{4+}. Working back from their reported Mo^{4+} content, assuming two K atoms are needed to convert one Mo^{VI} to one Mo^{IV}, we calculate K contents that are in the opposite order from what they report—*i.e.*, the red bronze, recalculated to $K_{0.34}MoO_3$, is relatively richer in K than is the blue, recalculated to $K_{0.29}MoO_3$. Curiously enough, the ideal formulas of the red and blue bronzes as worked out from the X-ray crystallographic analysis[3,4] are $K_{0.33}MoO_3$ and $K_{0.30}MoO_3$, respectively, in good agreement with the reducing power analysis. Both the K and the Mo analyses are difficult to carry out with great accuracy, so, given the fact that our results support the ideal crystallographically determined composition, we have chosen to use the ideal crystallographic descriptions for the rest of this communication. The blue bronze is assigned the formula $K_{0.30}MoO_3$; the red, $K_{0.33}MoO_3$.

The basic unit of the red bronze, $K_{0.33}MoO_3$, is a cluster of six distorted MoO_6 octahedra interlocked by edge-sharing to give Mo_6O_{18} stoichiometry. Two K^+ ions, resulting from the ionization of two K atoms, are associated with each cluster and the two valence electrons have been incorporated in the cluster. The basic unit of the blue bronze, $K_{0.30}MoO_3$, is a cluster of ten distorted MoO_6 octahedra interlocked by edge-sharing to give a $Mo_{10}O_{30}$ unit. There are three K^+ ions and hence three valence electrons incorporated per cluster. In both blue and red bronzes, clusters are interconnected by corner-sharing of octahedra through oxygens. Figure 4 gives a comparison of the red and blue structures, based on an idealized representation using regular octahedra instead of the distorted MoO_6 groupings actually observed.

The simplest model for K_xMoO_3 would be to assume that the K atom transfers its electron to a molybdenum atom to form an Mo^{V} center. The magnetic studies do not support such a model. Discrete Mo^{V} centers, as in MoX_6^-, $MoOX_4^-$, and $MoOX_5^{2-}$, generally show temperature-dependent paramagnetism[9] corresponding to $\mu_{eff} \approx 1.7$ BM. The observed low, temperature-independent magnetic susceptibility of the red bronze is more like the temperature-independent susceptibility of 50×10^{-6} cgs unit observed in polymeric $MoO_2X_2^-$ and $MoO_2(C_2O_4)^-$ compounds, where short Mo–Mo distances lead to direct interaction between the molybdenum atoms. It is probable that in the red $K_2Mo_6O_{18}$ bronze, the two electrons per cluster are spin paired because of occupancy of the same molecular orbital. (Even with distortion of the MoO_6 octahedra, the 4d t_{2g} orbitals of the Mo atoms could overlap each other through the shared octahedral edges so as to give MO's delocalized over several Mo atoms.) Simple spin pairing, however, would give diamagnetism, so, to explain the temperature-independent paramagnetism observed it would be necessary to postulate accessible excited states in which the spins could be uncoupled. Such an arrangement of isolated cluster orbitals would also account for the low conductivity exhibited by the red bronze. The feeble semiconduction observed would correspond to activated hopping of electrons from one cluster to another.

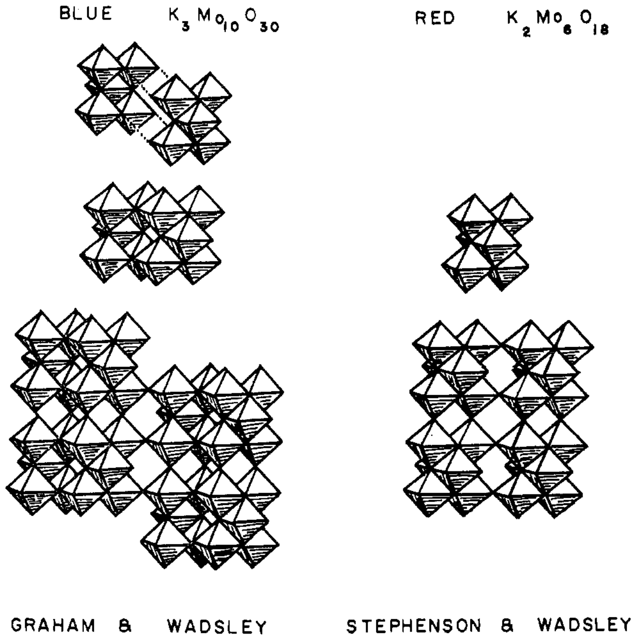

Figure 4.—Idealized structures of red and blue KMo bronzes. Actually, the MoO_6 octahedra are considerably distorted.

The blue bronze poses a more difficult problem. The lower magnetic susceptibility and the good conductivity at room temperature suggest a metallic model in which electrons are delocalized and mostly paired as a Pauli paramagnetic degenerate electron gas. However, both the Seebeck effect and the Hall effect indicate p-type carriers at room temperature. This makes a straightforward interpretation difficult. The magnitude of the observed Hall effect at room temperature corresponds to 4.2×10^{21} carriers/cc compared to 4.7×10^{21} K atoms/cc. It is not likely, however, that the p-type carriers are associated with "holes" originating from the K atoms. A more likely possibility is that the blue bronze represents a two-carrier system.

A two-carrier model is actually suggested by the

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(9) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 117 (1964).

unique changeover from n-type to p-type conduction as the temperature is raised. If the p-type carrier has a greater mobility than the n-type, then it can become dominant at higher temperature if its excitation energy is higher than that of the n-type carrier. A consistent model for blue KMo bronze would be that the low-temperature conductivity is dominated by electron hopping or electron excitation from donor centers into a narrow, low-mobility conduction band, while the high-temperature conductivity is dominated by hole conduction in a high-mobility valence band. The narrow conduction band could develop from small overlap of 4d t_{2g} orbitals between Mo atoms; the wide valence band, from large overlap of 4d t_{2g} Mo orbitals and oxygen $p\pi$ orbitals. Oxygen atoms that are bridge atoms between clusters could be centers for hole-type excitation, since removal of one electron from this site could make other binding electrons in the O–Mo–O–Mo–O molecular orbitals highly mobile. The two-carrier model suggests interesting photoconductive properties, and, indeed, a large photoconduction response has been observed.

The behavior of the Seebeck coefficient is qualitatively in agreement with the conductivity results. Below 180°K, Q is negative and rapidly becomes more negative as the temperature is decreased. Such a rapid decrease in Q is typical of an n-type semiconductor in which carrier density exponentially decreases with decreasing temperature. (For semiconductors, Q is roughly proportional to the reciprocal of the log of the carrier density.) Above 180°K, Q is very small and shows practically no change with temperature; this is consistent with metallic behavior. No special significance should be attached to the fact that Q is still negative in the range where the Hall voltage has already turned positive. It is not unusual (*cf.* NiO, Cu_2O) to have opposite signs for Q and the Hall voltage, particularly when phonon drag is important. The rather steep change to a substantial positive Q at 298°K, although consistent with p-type carriers, is not understood at the present time. It will be investigated further.

There is the final possibility that the observed changes are associated with structural changes in the critical regions $140°\text{K} < T < 180°\text{K}$ and 292–298°K. Dta analysis, however, with equipment sensitive to 0.0001 cal, showed no first-order changes and only the barest trace of a second-order change at about 160°K.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
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The Crystal Chemistry of Selected AB_2 Rare Earth Compounds with Selenium, Tellurium, and Antimony[1]

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The rare earth ditellurides, diselenides, and diantimonides were synthesized and their crystal structures were investigated. The ditellurides are isostructural and have the Fe_2As (C38) structure. The phases $HoTe_2$ and $ErTe_2$ do not exist and reasons for their absence are given. The structures of the diselenides display two types of supercells. The lighter rare earths have a tetragonal cell and the heavier ones have an orthorhombic cell, but the subcell has an arrangement which is identical with the telluride structure. The diantimonides are formed by a limited number of rare earths and they crystallize with a new structure which, however, is closely related to the $RETe_2$ type and to the $ZrSi_2$ structure. The phase $YbSb_2$ crystallizes in the latter type. The interrelationships among these structures and the nature of the bonding existing in these compounds is discussed.

Introduction

The stoichiometry REB_2, where RE is a rare earth element and B an element of groups V and VI, is widely encountered in such alloys. A structural investigation of these phases was undertaken, using single-crystal X-ray diffraction techniques wherever feasible, to determine their crystal structures and resolve any ambiguities which have arisen because of previous work which was based only on powder diffraction diagrams.

Rare earth diselenides were first prepared by Benacerraf, *et al.*,[2] and from chemical analyses they assigned the formula RE_2Se_4 to the La, Ce, Pr, and Nd compositions and the formula $RE_2Se_{3.6}$ to compounds of Sm and Gd. Powder patterns indicated that the unit cell was tetragonal and the lattice constants were determined. Vickery and Muir[3] studied $GdSe_2$ and reported that a low-temperature modification of this phase had the $ThSe_2$ type of structure. Veale and Barrett[4] found that in the Gd–Se system the phase exists only over the stoichiometry range $GdSe_{1.775-1.862}$ and the powder pattern cannot be indexed on an orthorhombic unit cell similar to $ThSe_2$ but has a tetragonal unit cell. Many diselenides and ditellurides display a solid solution

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[1] Research sponsored by Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, Grant No. 806-65.

[2] A. Benaceraff, L. Domange, and J. Flahaut, *Compt. Rend.*, **248**, 1672 (1959).

[3] R. C. Vickery and H. M. Muir, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p 223.

[4] C. R. Veale and M. F. Barrett, *J. Inorg. Nucl. Chem.*, **28**, 2161 (1966).