

be joined to each other by an oxygen atom or they may be entirely separated. An even greater possibility of distribution of the three vanadium atoms within the heteropoly cage exists for the 9-molybdo-3-vanadophosphate anion. No evidence for such isomerism was found in this work although it may well exist.

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Magnetic Susceptibility of Barium Molybdate(IV) and Strontium Molybdate(IV) in the Range 2–300°K¹

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The compounds BaMoO₃ and SrMoO₃ have been prepared by hydrogen reduction of the corresponding molybdates(VI). Magnetic susceptibilities, measured by the Gouy method, are positive, moderately large, and independent of temperature over almost the entire range between liquid helium and room temperature. After correction for diamagnetic constituents, the molar magnetic susceptibilities are 215×10^{-6} cgs unit at 290°K for BaMoO₃ and 201×10^{-6} cgs unit at 291°K for SrMoO₃. These values are considerably higher than expected on the basis of a free-electron gas model that would be consistent with the high metallic conductivity and low Seebeck effect observed. A narrow d-band model with nonparabolic density-of-states filling seems to be indicated, with the Fermi energy apparently lying at a minimum in the density-of-states curve.

Introduction

The transition metal oxide bronzes have proven to be valuable sources of information on the important problem of electron transport and magnetic interaction in transition metal oxides. The tungsten bronzes, M_xWO₃, are slightly paramagnetic and metallic; the vanadium bronzes, M_xV₂O₅, are magnetic and semiconducting.² Titanium bronzes, Na_xTiO₂,³ and niobium bronzes, Sr_xNbO₃,⁴ though less well investigated, also apparently show metallic properties. Thus, there is a crude periodic correlation in that moving down a group or to the left in a period favors the appearance of metallic behavior. The molybdenum bronzes, M_xMoO₃, are particularly interesting since they appear to be close to the line of semiconductor-to-metal transition. Blue potassium molybdenum bronze, K_{0.30}MoO₃, for example, shows a curious mixture of metallic paramagnetism and semiconductive-to-metallic conductivity.⁵ When, in connection with another investigation, we had occasion to synthesize samples of the metallic molybdates BaMoO₃ and SrMoO₃, it was thought useful to measure their magnetic

susceptibility properties in the hope of gaining more insight into the nature of their electronic structure. Although they do not deviate from stoichiometry and, therefore, are perhaps not classifiable as true bronzes, they represent an important reference point in the series.

Experimental Section

Preparation of Samples.—The compounds were prepared by the hydrogen reduction method of Scholder and Brixner.⁶ BaMoO₄ and SrMoO₄ were made by precipitation from pH 10 aqueous solutions of (NH₄)₂MoO₄ with the appropriate alkaline earth nitrate. After being dried overnight and fired in air to constant weight at 800°, the molybdates were heated under a slow stream of 85% argon–15% hydrogen in scrupulously clean platinum boats. Reduction time was about 8–12 hr, at 950° for SrMoO₃ and 1000° for BaMoO₃. Completeness of the reduction was monitored by weight loss and confirmed by weight gain on reoxidation. Agreement in each case was within 0.1% of the theoretical. X-Ray pictures taken with Cu K α radiation gave unit-cell spacings of 4.040 Å for BaMoO₃ and 3.975 Å for SrMoO₃ in agreement with the reported values of Brixner.⁷ Both materials were found to be highly conducting.

Magnetic Measurements.—The apparatus was the same Gouy balance and cryogenic setup previously described.⁸ Tubes were of quartz, 4 mm in diameter, and were filled to a height of about 20 cm. Forces were measured with a Mettler H-6 microbalance over a field range from 1000 to 6000 G. Susceptibilities showed a slight field dependence (11% for BaMoO₃ and 13% for SrMoO₃) compared to NiCl₂ standard, so values of χ were extrapolated to zero reciprocal field. The slopes of χ vs. H^{-1} were about 13% greater at liquid helium temperature than at room temperature. Reproducibility of the extrapolated susceptibility at liquid

(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. 796-67 and was supported in part by the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

(2) The properties and structures of the tungsten and vanadium bronzes are reviewed in: R. P. Ozerov, *Usp. Khim.*, **24**, 951 (1955); M. J. Sienko, "The Alkali Metals," Special Publication No. 22, The Chemical Society, London, 1967, p 429; M. J. Sienko, *Advances in Chemistry Series*, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

(3) A. F. Reid and M. J. Sienko, *Inorg. Chem.*, **6**, 321 (1967).

(4) D. Ridgley and R. Ward, *J. Am. Chem. Soc.*, **77**, 6132 (1955).

(5) G. H. Bouchard, Jr., J. Perlstein, and M. J. Sienko, *Inorg. Chem.*, **6**, 1682 (1967).

(6) R. Scholder and L. H. Brixner, *Z. Naturforsch.*, **10b**, 178 (1955).

(7) L. H. Brixner, *J. Inorg. Nucl. Chem.*, **14**, 225 (1960).

(8) M. J. Sienko and J. Sohn, *J. Chem. Phys.*, **44**, 1369 (1966).

helium temperature was better than 6%. The observed susceptibilities are believed to be accurate to better than 15%. Corrections for diamagnetism, taken from Selwood,⁹ were as follows (per g-ion): Ba²⁺, -32×10^{-6} ; Sr²⁺, -15×10^{-6} ; Mo⁴⁺, -17×10^{-6} ; O²⁻, -12×10^{-6} .

Results and Discussion

At 290°K, the net paramagnetic susceptibility (in cgs unit per mole) was 201×10^{-6} for SrMoO₃ and 215×10^{-6} for BaMoO₃. These values remained constant within 3% almost down to liquid helium temperatures. At very low temperatures, a considerable rise in SrMoO₃ susceptibility was observed—e.g., from 241×10^{-6} at 4.17°K to 329×10^{-6} at 1.21°K. For BaMoO₃, the low-temperature rise was considerably smaller—e.g., from 210×10^{-6} at 4.26°K to 223×10^{-6} at 1.26°K. Thus, except at 4°K and below, the paramagnetic susceptibility appears to be nearly temperature independent, in gratifying agreement with the prediction of Goodenough¹⁰ that the behavior should correspond to that of a Pauli-type electron gas. However, the value observed is almost an order of magnitude greater than expected.

Brixner, in his study of the X-ray scattering and electrical properties of the system Ba_xSr_{1-x}MoO₃,⁷ found that all of the members of the series exhibited low electrical resistivity (50–80 μohm cm on sintered-powder specimens) and a small Seebeck coefficient (few microvolts per degree). Given that powder resistivities are invariably greater than true crystal resistivity, it is evident that only a metallic model could be valid for these materials. Our magnetic results confirm this conclusion, since a localized d-electron model would predict for Mo⁴⁺ (4d²) magnetic moments of the order of 2 or 3 BM, corresponding to room-temperature susceptibilities of the order of 3000×10^{-6} , and a strong Curie–Weiss type of dependence on temperature. The moment could be brought down by postulating antiferromagnetic exchange coupling, but the lack of temperature dependence would be difficult to reconcile as would the obvious metallic behavior.

The simplest model for BaMoO₃ and SrMoO₃ would be the one that has been used so successfully for the tungsten bronzes—*viz.*, Ba or Sr acts as an interstitial donor in a MoO₃ host structure to contribute two valence electrons to the collective electron assembly. Assuming two such free electrons from each Ba atom we would calculate in BaMoO₃ a total free electron density of 3.04×10^{22} electrons/cc. Such an electron density would lead to a volume susceptibility χ of about 0.68×10^{-6} /cc, even neglecting the Landau term ($-m_0^2/3m^{*2}$) in the computation

$$\chi = \frac{4m^*\mu_0^2}{h^2}(3\pi^2n)^{1/3}\left(1 - \frac{m_0^2}{3m^{*2}}\right)$$

Here μ_0 is the Bohr magneton, n is the electron density, and m^* , the effective mass, has been taken equal to the electronic rest mass m_0 . With a molar volume of 39.7 cc for BaMoO₃, the molar Pauli susceptibility would

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

(10) J. B. Goodenough, *Czech. J. Phys.*, **B17**, 304 (1967).

amount to only 27×10^{-6} , compared to the 200×10^{-6} observed. The effective mass would need to be about eight times the rest mass, rather high for the simple-band picture to apply. Also, such high effective mass should manifest itself in the conductivity and the Seebeck effect.

Powder conductivity data are always subject to suspicion, but Brixner's finding of an almost linear rise of resistivity with temperature suggests that his values might have some quantitative significance. In any event, his quoted value of 53×10^{-6} ohm cm for the specific resistivity of BaMoO₃ gives an upper limit. Assuming that the specific conductivity σ is given by $ne\mu$, where μ is the electronic mobility, we calculate a mobility of about 4 cm²/V sec. Given that this value is only a lower limit but already is approaching the 10–20-cm²/V sec value found in the tungsten bronzes, it appears that nearly free carriers are involved.

The Seebeck effect is more complicated. For BaMoO₃, the measured value was reported as 4.00 μV/deg, with copper leads and the lead to the hot junction negative.¹¹ Using the convention that the Seebeck coefficient Q is positive for the junction A–B when positive current goes from A to B at the cold junction,¹² we have $Q(\text{BaMoO}_3\text{-Cu}) = +4.00 \mu\text{V/deg}$. Since $Q(\text{A-B}) = Q^0(\text{A}) - Q^0(\text{B})$, where Q^0 represents the absolute thermal emf, we can write for the absolute thermal emf of BaMoO₃

$$Q^0(\text{BaMoO}_3) = Q(\text{BaMoO}_3\text{-Cu}) + Q^0(\text{Cu})$$

Combining the observed Q of the BaMoO₃–Cu junction, +4.00 μV/deg, with the absolute thermal emf of copper,¹³ +1.73 μV/deg, at 0° we get +5.73 μV/deg for the absolute thermal emf observed for BaMoO₃. This is to be compared with a value of $-4.14 \mu\text{V/deg}$ calculated for a highly degenerate electron gas¹⁴

$$Q = -86.2(r + 1)\frac{\pi^2}{3}(kT/E_F)$$

where $r = 1$ for an ionic lattice and E_F , the Fermi energy, is given by $[(3\pi^2n)^{2/3}h^2]/(8\pi^2m)$. The sign discrepancy between the observed +5.73 and the calculated -4.14 emf value of BaMoO₃ is not a valid reason for rejecting a metallic model for it, since positive thermal emf's are quite generally found for even very good metals. For example, the absolute thermal emf of metallic lithium is +11.5 μV/deg whereas that of metallic sodium is $-8.3 \mu\text{V/deg}$.

Conduction band states in BaMoO₃ could be made up of 4d (t_{2g}) wave functions of the molybdenum atoms or from the antibonding combinations of the Mo 4d (t_{2g}) functions and the $p\pi$ of the intervening oxygen atoms.¹⁰ The magnetic data do not allow us to choose between the two alternatives. The rather large sus-

(11) L. H. Brixner, private communication.

(12) See, for example, D. K. C. MacDonald, "Thermoelectricity," John Wiley and Sons, Inc., New York, N. Y., 1962, p 2.

(13) "Landolt-Bornstein Zahlenwerte und Funktionen," Vol. II, 6th ed, Part 6, Springer-Verlag, Berlin, 1959, p 931.

(14) See, for example, J. B. Sohn, Ph.D. Thesis, Cornell University, 1965, p 105.

ceptibility suggests that the band is narrow and has a high density of states. Further grounds for choosing between Mo–Mo and Mo–O–Mo* orbitals might come from a study of mobility values. However, to be meaningful, mobility values would need to be determined on single-crystal specimens.

Another parameter that would be valuable for defining the electronic states in the molybdenum bronzes is the electronic heat capacity and its implied information about density of states. BaMoO₃, with $d\chi/dT$ equal to zero, appears to represent a metal in which the two opposing effects contributing to $d\chi/dT$ just cancel each other out. These two effects are (I) variation with temperature of the width of the Fermi distribution and (II) variation with temperature of the Fermi energy itself. As remarked by Kriessman and Callen,¹⁵ the alternation of sign(+, −, +, −, +) observed for $d\chi/dT$ in the sequence Ti, V, Cr, Mn, (Ru) matches the oscillation of magnetic susceptibility and electronic specific heat in these elements, presumably because of the sequence of maxima and minima in the density-

of-states curve. At low temperatures, contribution (II) to $d\chi/dT$ is always negative, so contribution (I) must be positive for BaMoO₃. This would be the case if the Fermi energy in BaMoO₃ lies near a minimum in the density-of-states curve, as is true for titanium and presumably also for zirconium. Compared to metals in general, then, BaMoO₃ should show a moderately high electronic specific heat. Also if BaMoO₃ corresponds to electron-filling at a minimum in the density-of-states curve, a reduction in carrier density would move the Fermi level to higher density of states, thereby leading to a larger electronic specific heat and a larger magnetic susceptibility. These predictions might be open to experimental verification by systematic study of Brixner's series SrMo_xZr_{1-x}O₃ and SrMo_xTi_{1-x}O₃.¹⁶ Both the conductivity and the Seebeck effect of these materials change so as to suggest that substitution of Zr or Ti for Mo reduces carrier density. Systematic substitution of Zr (or Ti) for Mo and study of the magnetic susceptibility and specific heat as a function of temperature would provide valuable data for defining a density-of-states curve.

(15) C. J. Kriessman and H. B. Callen, *Phys. Rev.*, **94**, 837 (1954).

(16) L. H. Brixner, *J. Inorg. Nucl. Chem.*, **15**, 356 (1960).

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High-Pressure NaAlO₂, an α -NaFeO₂ Isotype

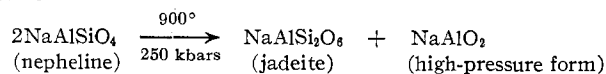
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The β form of sodium aluminate has been transformed at 110 kbars and 900° to a new high-pressure form isostructural with rhombohedral α -NaFeO₂. The increase in density from 2.74 to 3.61 g cm⁻³ corresponds to a change from tetrahedral to octahedral coordination for all atoms in the structure. The new phase has three molecules in a hexagonal unit cell with dimensions $a = 2.868 \pm 0.005$ Å and $c = 15.88 \pm 0.01$ Å. The space group is R3m, with sodium atoms in positions 3(a), aluminum atoms in 3(b), and oxygen atoms in 6(c) with atomic coordinates (0, 0, 0.228). Aluminum–oxygen distances are 1.92 ± 0.05 Å, and sodium–oxygen distances are 2.35 ± 0.05 Å. The present study confirms that this new form of sodium aluminate together with jadeite, NaAlSi₂O₆, are the products of dissociation of nepheline, NaAlSiO₄, at pressures in the region 100 to 200 kbars.

Polymorphic transformations of minerals are believed to be responsible for density increases in the upper mantle of the earth at depths of some several hundred kilometers.¹ We have recently shown² that synthetic potassium feldspar (sanidine), KAlSi₃O₈, transforms at 900° and 120 kbars to the dense hollandite structure, with randomly distributed six-coordinated aluminium and silicon. Various investigations have shown³ that high pressures favor denser phases containing octahedral rather than tetrahedral aluminium. A recent example⁴ is the transformation at high pressure of

NaAlGeO₄, a low density analog of NaAlSiO₄ (nepheline), to the much denser calcium ferrite structure⁵ with Al³⁺ and Ge⁴⁺ randomly distributed in octahedral positions.⁴ NaAlSiO₄ should itself ultimately transform to the calcium ferrite structure, but at pressures as high as 250 kbars it was found⁶ to disproportionate to jadeite and a new phase according to the proposed reaction



The iron compound behaved similarly and gave NaFeSi₂O₆ (acmite, isomorphous with jadeite) plus a phase assumed to be NaFeO₂.

(1) F. Birch, *J. Geophys. Res.*, **57**, 227 (1952).
(2) A. E. Ringwood, A. F. Reid, and A. D. Wadsley, *Acta Cryst.*, **23**, 1093 (1967).
(3) F. Datchile and R. Roy in "Modern Very High Pressure Techniques," R. H. Wentorf, Ed., Butterworth and Co. Ltd., London, 1962, Chapter 9.
(4) A. F. Reid, A. D. Wadsley, and A. E. Ringwood, *Acta Cryst.*, **23**, 738 (1967).

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(6) A. E. Ringwood and A. Major, *Earth Planetary Sci. Letters*, **2**, 106 (1967).