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†Present address: Physics Department, University of Virginia, Charlottesville, Va. 22903

¹R. S. Krishnan, Proc. Indian Acad. Sci. 24, 25 (1946).

²S. A. Solin and A. K. Ramdas, Phys. Rev. (to be published).

³M. Wortis, Phys. Rev. 132, 85 (1963); J. Hanus, Phys. Rev. Letters 11, 336 (1963).

⁴J. B. Torrance, Jr., U. S. Office of Naval Research

Project No. NR-018-407, Harvard University, Technical Report No. 1 (unpublished).

⁵The derivation of the two-phonon Hamiltonian and the subsequent theoretical development of the present work will be presented in more detail in a future publication. For a general treatment of anharmonic effects in crystals see, for example, G. Leibfried and W. Ludwig, Solid State Phys. 12, 276 (1961).

⁶Upon neglect of umklapp processes, $\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4 = \vec{K}$, the total wave vector. Diagonalization of Eq. (1) would lead to a full two-phonon energy spectrum $E_2(K)$. We restrict ourselves here to the bound states with $\vec{K} = 0$; the dispersion relations for bound states with $\vec{K} \neq 0$ will be presented elsewhere.

⁷R. M. Martin, Chem. Phys. Letters 2, 268 (1968).

⁸R. G. Parr and R. F. Borkman, J. Chem. Phys. 46, 3683 (1967); R. F. Borkman and R. G. Parr, J. Chem. Phys. 48, 1116 (1968).

MEASUREMENT OF THE de HAAS-van ALPHEN EFFECT IN PEROVSKITE-TYPE MOLYBDENUM BRONZES $A_x\text{MoO}_3$

S. M. Marcus and T. A. Bither

Central Research Department, E. I. du Pont de Nemours and Company,
Experimental Station, Wilmington, Delaware 19898

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The de Haas-van Alphen effect has been detected in the cubic perovskite-type bronzes $\text{Na}_{0.93}\text{MoO}_3$ and $\text{K}_{0.92}\text{MoO}_3$. These are the first observations of this effect in grossly nonstoichiometric compounds.

We wish to report our observations of the de Haas-van Alphen effect in the molybdenum bronzes $\text{Na}_{0.93}\text{MoO}_3$ and $\text{K}_{0.92}\text{MoO}_3$ which have the cubic perovskite-type structure.^{1,2} These are the first observations of this effect in grossly nonstoichiometric compounds.

The compounds we have measured are isotypes of the tungsten bronzes³ with molybdenum replacing the tungsten atom in the *B* position. The NMR studies on cubic Na_xWO_3 by Fromhold and Narath⁴ lead them to conclude that these sodium-tungsten bronzes have a strong *d* character for the conduction states and a negligibly small density of sodium states near the Fermi level. The sodium atoms form Na^+ ions and donate their valence electrons to the *5d* tungsten conduction band. In a subsequent NMR study⁵ of the isotype ReO_3 , they conclude that the conduction-band states near the Fermi level are very similar to those of Na_xWO_3 .

In MoO_3 the Mo^{+6} ion has no *4d* electrons, whereas in ReO_3 the Re^{+6} ion has a *5d*¹ configuration. If we add the number of electrons supplied to the *4d* band by the alkali atoms at the *A* sites, the number of electrons in the *d* bands of these three compounds is approximately equal, i.e., 1,

0.92, and 0.93 electrons per molecule for ReO_3 , $\text{K}_{0.92}\text{MoO}_3$, and $\text{Na}_{0.93}\text{MoO}_3$, respectively. In the bronzes the alkali atoms have their lowest band several volts above the Fermi level⁶; therefore, not only is the character of the bands at the Fermi level insignificantly affected by the *A*-site atoms,⁴ but the conduction electrons should not be appreciably scattered by these atoms. We therefore expect the Fermi sheets of the molybdenum bronzes to be similar to those of ReO_3 ⁷ and the strengths of the de Haas-van Alphen signals to be comparable.

The single crystal of $\text{K}_{0.92}\text{MoO}_3$ ($\text{Na}_{0.93}\text{MoO}_3$) was grown at 65 kbars in a tetrahedral anvil press¹; the room-temperature resistivity was 1.3×10^{-5} (1.6×10^{-5}) Ω cm; the resistivity ratio $\rho(\text{rm.})/\rho(4.2^\circ\text{K})$ was 57 (200); the cell dimension a_0 at room temperature was 3.919 (3.850) \AA . Guinier x-ray diffraction powder patterns made at room temperature on other crystals from the same preparative runs showed single-phase materials having the cubic perovskite-type crystal structure. The de Haas-van Alphen measurements were performed by field modulation to maximum fields of 50 kG and generally at 1.1°K. This equipment has been more fully described in

a previous paper by Marcus and Donohue.⁸

I. $K_{0.92}MoO_3$.—The de Haas–van Alphen frequencies of $K_{0.92}MoO_3$ were measured with H in the (100) and (1 $\bar{1}$ 0) crystallographic planes. At all orientations, two frequencies associated with two de Haas–van Alphen branches (K_1, K_2) were observed. These observed frequencies as a function of field orientation are shown in Fig. 1(a).

K_1 has a minimum value of 4.47×10^7 G at [001], increasing to a maximum of 5.16×10^7 G at [011], and within experimental error has the same maximum value at [111]. The mass of the carriers associated with this branch at [001] is $0.78m_e$ (m_e is the mass of the electron). This branch generally predominates in the signal.

K_2 has a minimum frequency of 5.5×10^7 G at [001], increasing to a maximum value of 6.9×10^7 G at [111]. Its value at [110] is 6.3×10^7 G.

Both branches are consistent with cubic symmetry, as expected for this perovskite-type bronze.

II. $Na_{0.93}MoO_3$.—The de Haas–van Alphen frequencies of $Na_{0.93}MoO_3$ were measured with H in the (100) crystallographic plane. The measured frequencies fall into two groups, low-frequency oscillations in the 10^6 -G range and higher-frequency oscillations in the 10^7 -G range. These observed frequencies as a function of field orientation

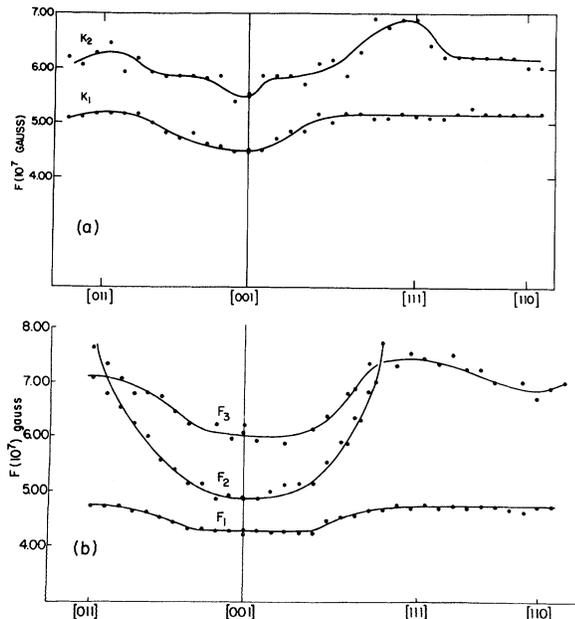


FIG. 1. (a) de Haas–van Alphen frequencies of $K_{0.92}MoO_3$; H in (100) and (1 $\bar{1}$ 0) planes. (b) de Haas–van Alphen frequencies of ReO_3 ; H in (100) and (1 $\bar{1}$ 0) planes.

tation are shown in Fig. 2.

A. Low-frequency oscillations.—A single frequency branch was observed in going from [001] to 7° past [011]. The value of the branch at [001] is 0.51×10^6 G and increases to 1.5×10^6 G at 20° past [011]. At 7° past [011] a second frequency is observed approximately two orders of magnitude lower in amplitude than the first frequency. At 12° from [011] the amplitudes of both signals have become approximately equal. In the angular range 12° to 22° from [011] both signals are comparable, and beyond this region toward [010] only the second signal is observed. Within experimental error the frequencies measured at [010] and [001] are equal. The low-frequency branches dominated the signal below 20 kG and were detected in fields as low as 6 kG. The mass of the carriers associated with the branch at [001] is $0.11m_e$. These frequencies are shown in the lower part of Fig. 2.

In order to be consistent with cubic symmetry, the measured frequencies as a function of orientation should be symmetrical about [011]. We would then expect the frequencies on both a and a' to be present, where a' is obtained by reflecting a through [011]. Since the expected frequencies associated with the dashed portion of a' were not detected, the sample was misoriented and re-measured to see whether the above results would be modified. With H near [011], data were taken with H tilted out of the (100) plane by approximately 4° and at temperatures of 1.1 and 4.2°K.⁹ No observable changes in frequency were detected for a given orientation in measurements at these two temperatures. In addition, no significant changes in frequency or amplitude of signal

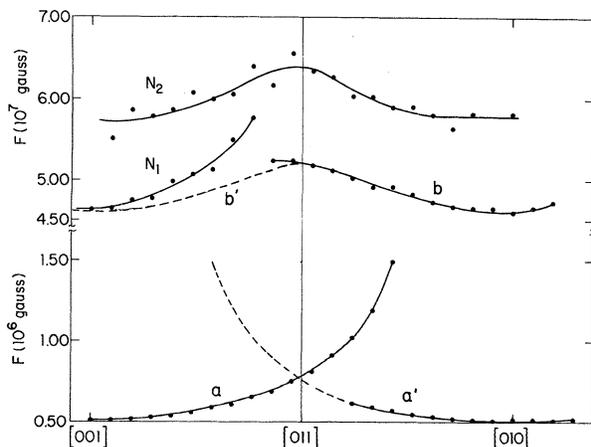


FIG. 2. de Haas–van Alphen frequencies of $Na_{0.93}MoO_3$; H in (100) plane.

were observed for comparable orientations when H was rotated in the (100) plane and when H was rotated in a plane tilted approximately 4° to the (100) plane. We, therefore, must conclude that cubic symmetry is not satisfied in these branches to at least 4.2°K .

B. High-frequency oscillations.—At all orientations, two frequencies which are associated with two de Haas–van Alphen branches were observed (N_1, N_2).

N_1 has a minimum value of 4.65×10^7 G at [001] and [010], increasing to 5.26×10^7 G from [010] to [011]. In going from [001] toward [011], the frequency increases but does not have the same behavior as the frequency in the angular range between [010] and [011]. The dashed curve b' is b reflected through [011]. In comparing that part of N_1 which is to the left of [011] with b' , we conclude that N_1 is not consistent with cubic symmetry. The mass of the carriers associated with this branch at [001] is $0.81m_e$.

N_2 has a minimum value of 5.8×10^7 G at [001] and [010] and increases to a maximum value of 6.5×10^7 G at [011]. Within experimental error this branch is consistent with cubic symmetry.

In comparing the de Haas–van Alphen branches of $\text{K}_{0.92}\text{MoO}_3$ with those of $\text{Na}_{0.93}\text{MoO}_3$, we observe similarities between their higher frequency branches. The frequencies of K_1 and N_1 , as well as of K_2 and N_2 , are within 5% of each other when H is parallel to [001] and [011] (Table I). The measured masses are also similar; i.e., for H parallel to [001] the mass of the carriers associated with K_1 is $0.78m_e$, compared with a mass of $0.81m_e$ for N_1 . The dissimilarities between the branches of these two compounds are that while K_1 is consistent with cubic symmetry, N_1 is not, and the low-frequency oscillations observed in $\text{Na}_{0.93}\text{MoO}_3$ are not present in $\text{K}_{0.92}\text{MoO}_3$.

The noncubic character of the branches in $\text{Na}_{0.93}\text{MoO}_3$ may be due to a distortion of the crystal from cubic symmetry. This would be very small, however, as x-ray data show this crystal to satisfy cubic symmetry.⁹

III. ReO_3 .—The de Haas–van Alphen frequencies of ReO_3 as measured by Marcus¹⁰ are shown in Fig. 1(b). The measurements were taken with H in the (100) and (110) crystallographic planes. Three branches were observed (F_1, F_2, F_3), and all are consistent with cubic symmetry.

F_1 and F_3 are associated with orbits located on approximately spherical Fermi sheets centered on Γ in the cubic zone. F_2 is associated with an orbit located on an open sheet centered on Γ with

Table I. Frequencies of the branches $N_1, N_2; K_1, K_2$; and F_1, F_2 for $\text{Na}_{0.93}\text{MoO}_3, \text{K}_{0.92}\text{MoO}_3$, and ReO_3 , respectively, with H along major crystallographic directions.

Branch	F for given orientation (10^7 G)		
	[001]	[011]	[111]
N_1	4.65	5.26	
K_1	4.47	5.16	5.16
F_1	4.20	4.75	4.75
N_2	5.8	6.5	
K_2	5.5	6.3	6.9
F_3	6.0	7.0	7.5

arms along the cubic axis.⁷

In order to compare the Fermi sheets of the molybdenum bronzes with those of ReO_3 , the compound $\text{K}_{0.92}\text{MoO}_3$ will be used since the de Haas–van Alphen branches of both of these materials satisfy cubic symmetry. Comparing the branches observed in $\text{K}_{0.92}\text{MoO}_3$ [Fig. 1(a)] with those observed in ReO_3 [Fig. 1(b)], it is seen that K_1 has the same general shape as that of F_1 and the frequencies are within 10% of each other. The same can be said of K_2 and F_3 . The measured frequencies for H parallel to the major crystallographic axis are listed in Table I. The measured masses in these two compounds are also similar; i.e., the mean value of the mass of the carriers associated with F_1 is $0.67m_e$, compared with a mass of 0.78 for K_1 measured at [001]. A further similarity is that the strength of the de Haas–van Alphen signals in the molybdenum bronzes compares in amplitude with that of the signal observed in ReO_3 . A dissimilarity between the molybdenum bronzes and ReO_3 is that in the bronzes no branch was observed which could be associated with F_2 in ReO_3 . A possible explanation for this could be that a significantly higher mass is associated with this branch than that associated with F_2 , thus reducing its signal to an undetectable level in our measurements.

These similarities in the de Haas–van Alphen branches, masses, and signal amplitudes thus support the conclusions of Narath and Barham⁵ and the calculation of Mattheiss⁶ that (1) the conduction bands of the bronzes and ReO_3 near the Fermi level are essentially equivalent, and (2) the alkali ions of the A position in the bronzes have their bands sufficiently removed from the Fermi level to cause insignificant modification of the conduction bands or scattering of the con-

duction electrons.

We wish to thank Mr. James Moore for his help in taking and analyzing these data.

¹T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.* **5**, 1559 (1966).

²The perovskite-structure type, with the general formula ABO_3 , has a cubic unit cell with the A atom located at the corners, the B atom at the center, and the O atoms at the face centers of the cube. In the non-stoichiometric bronzes (the best-known member of this class is the sodium-tungsten bronze Na_xWO_3), the A position is only partially (and in general randomly) occupied, while the B site is filled by a transition metal. In the related cubic compound ReO_3 , the A position is empty and the B position is occupied by Re .

³Efforts to prepare crystals of Na_xWO_3 having resistivity ratios sufficiently high to allow observations of the de Haas-van Alphen effect were unsuccessful. Resistivity ratios ≤ 16 were obtained on crystals prepared both by melt fusion and hydrothermal techniques.

⁴A. T. Fromhold and A. Narath, *Phys. Rev.* **152**, 585 (1966).

⁵A. Narath and D. C. Barham, *Phys. Rev.* **176**, 479 (1968).

⁶L. F. Mattheiss, private communication.

⁷L. F. Mattheiss, *Phys. Rev.* **181**, 987 (1969).

⁸S. M. Marcus and P. C. Donohue, *Phys. Rev.* **183**, 668 (1969).

⁹X-ray diffractometer powder patterns were taken on $Na_{0.93}MoO_3$ at room temperature and at 4.2°K. No deviations from crystallographic cubic symmetry were observed at 4.2°K.

¹⁰S. M. Marcus, *Phys. Letters* **27A**, 584 (1968).

MOTT TRANSITION IN Cr-DOPED V_2O_3

D. B. McWhan, T. M. Rice, and J. P. Remeika

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

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A first-order metal-insulator transition at room temperature has been found in Cr-doped V_2O_3 as a function of both Cr concentration and pressure. This is shown to be a Mott transition in which the conduction electrons localize to form the insulator. A generalized phase diagram relating the metallic, insulating, and antiferromagnetic insulating phases is presented.

A sharp metal-insulator transition has been found in Cr-doped V_2O_3 as a function of both Cr concentration and pressure at room temperature. There is no change in the long-range order at the transition and, from a study of the entropy and susceptibility, it is inferred that the insulating phase has local moments. We conclude that this is an example of a transition in which the conduction electrons localize to form an insulator as predicted on theoretical grounds by Mott in 1949.^{1,2} It is postulated that the metal-insulator (M-I) phase boundary terminates at higher temperatures at a critical point. At lower temperatures the local moments order to form an antiferromagnetic (AF) state.³⁻⁵ In pure V_2O_3 we identify the high-temperature anomaly⁶ as a continuous M-I transition above the critical point, and the sharp discontinuity in electrical resistivity at low temperatures with the M-AF transition.⁷

Striking anomalies occur in the c/a ratio of the lattice parameters of the corundum structure as a function of the transition metal (see inset in Fig. 1).⁸ From a study of single-crystal samples in the system $(V_{1-x}Cr_x)_2O_3$ we find that a sharp

drop in c/a and a volume expansion of 1% occurs at $x=0.009$. At room temperature pure V_2O_3 is a poor metal (resistivity $\sim 10^{-3} \Omega \text{ cm}$), and an addition of a few percent Cr raises the resistivity several orders of magnitude.⁹ Below we report extensive measurements made on single-crystal rhombohedral prisms of $(V_{1-x}Cr_x)_2O_3$ with $x=0, 0.01, 0.02, 0.04$, and 0.10, which were prepared by a new technique.

The results of some of our x-ray diffraction measurements as a function of temperature are shown in Fig. 1. For $T \geq 600^\circ\text{K}$, V_2O_3 and the 4%-Cr-doped sample have similar c/a ratios. The ratio in the Cr-doped sample increases smoothly down to the Néel temperature, whereas in V_2O_3 there is an anomaly in c/a at high temperature corresponding to that found in the resistivity. A refinement of the crystal structures of V_2O_3 and $(V_{0.96}Cr_{0.04})_2O_3$ at room temperature shows that the overall volume and all nearest-neighbor vanadium-vanadium distances are larger in the Cr-doped sample.¹⁰ On cooling V_2O_3 through the M-AF transition we find that both a axes expand while c contracts, whereas the opposite occurs in the Cr-doped sample. (The gen-