Letters

On the Conductivity Character of $NbAs_2$-Type Compounds

In anion-rich compounds of the early 4d and 5d transition elements a trigonal-prismatic co-ordination of the cation is rather frequent. In such a co-ordination one of the five d-levels is considerably lowered energetically and therefore d^1 and d^2 cations prefer this environment. In the monoclinic structure of $NbAs_2$ [1], shown in fig. 1, the cations are also located inside a trigonal prism formed by the anions. However, the anion prisms are connected in pairs by sharing one square face. These double prisms are stacked to form infinite columns in the *b* direction (shortest axis). Each column is surrounded by two columns on the same level and also four columns shifted by *b*/2. This arrangement leads to pair formation of half the anions. Thus, only five cation valence electrons are needed to complete the valence shell of the anions. $NbAs_2$ and its isoelectronic analogues, therefore, might be normal valence compounds. As would follow from the ionic formula $Nb^{5+}\,As_I^{3-}$-As_{II}^{2-}, $NbAs_2$ is indeed diamagnetic [2] but its electrical conductivity is, nevertheless, metallic. The Seebeck coefficients of all $NbAs_2$ analogues are negative (table II), indicating that the predominant charge carriers are electrons. The occurrence of prism pairs appears to give rise to the formation of cation-cation bonds, which would account for the metallic properties. The Nb-Nb distance is 3.23Å in $NbSb_2$ [1], 3.01Å in $NbAs_2$ [1], and probably less than 2.9Å in NbP_2, which compares with an Nb-Nb bond distance of 2.90Å found in diamagnetic and non-metallic NbS_2Cl_2 [3], in which an Nb-Nb single bond is essential for its non-metallic character.

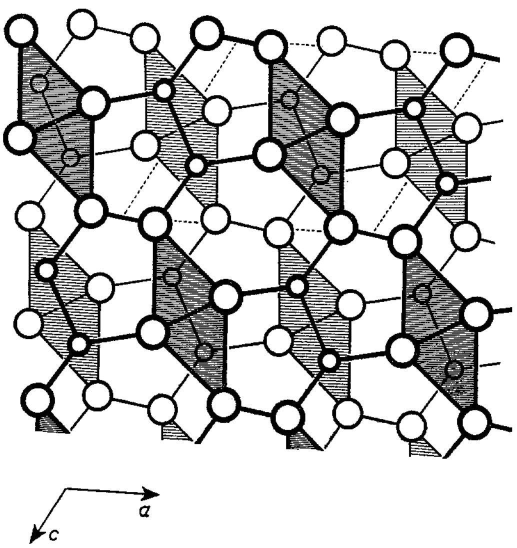

Figure 1 Projection of the structure of $NbAs_2$ along the *b*-axis, the direction of the trigonal-prism axes. Large circles: As.

In the $MoAs_2$ branch of the $NbAs_2$ family such cation-cation bonds would indeed be appropriate. In $MoAs_2$ and its analogues one more cation valence electron is available for bonding. Whereas in $NbAs_2$ cation pairs make a saturation of the chemical bonds impossible, such pairs would be necessary in order to produce non-metallic properties in $MoAs_2$, unless the As-As bonds would be loosened. However, there is no geometrical difference between $NbAs_2$ and $MoAs_2$, in which the corresponding distances are Mo-Mo = 2.98Å and As-As = 2.41Å [4]. Nevertheless, $MoAs_2$ single crystals also revealed a low electrical resistivity with a metallic temperature dependence. Thus, we assume that the electrical properties of these compounds are determined by a narrow d-band (overlapping the s,p-valence band), which may be almost empty in $NbAs_2$, but filled to a higher degree in $MoAs_2$. We may note that crystals of $NbAs_2$ and $MoAs_2$ both are brittle.

Various compounds with partially-filled d-bands have been found to be superconductors with reasonably high transition temperatures. Typical examples are ZrN [5], YSe [6], $RhSe_2$(h) [5], PtSbTe [7], $AuSb_2$ [5], CuS_2 [8], $CuRh_2S_4$ [9], Nb_3Se_4 [10] and $NbSe_2$ [11]. The excess or deficit of one electron ($\sim \frac{1}{3}$ in the case of Nb_3Se_4) is responsible for the metallic and superconductive character of these phases. Superconductors with d-electrons only are of interest because they may contribute to the knowledge of the relative importance of d- versus s,p-electrons for the occurrence of superconductivity in the transition metals. A recent theory [12] explains superconductivity in the transition metals to arise mainly from interactions between the s,p-electrons, mediated by screened plasma oscillations of the d-electrons. According to this theory the electron-phonon interaction is rather small for d-electrons, so that, in spite of the high density of states at the Fermi surface, the transition temperature would be very low in the absence of s,p-electrons. Therefore, we made checks for superconductivity in all known $NbAs_2$ isomorphs, to which we added the new ternary phases MoGeAs, WGeAs and ReGeAs (see table I). Powder samples were obtained by reacting the powdered high-purity elements in evacuated silica tubes at temperatures of between 700 and 900°C. Single crystals of $NbAs_2$, $TaAs_2$, $MoAs_2$, $NbSb_2$ and $TaSb_2$ were grown by a transport reaction using iodine or bromine as a carrier gas. The starting material was held at 950 to 1000°C while the crystals formed in a region which was about 50° cooler. The superconductivity tests down to 0.3K were made at 16 kc using an induction method, or with a magnetometer in the earth field. The tests in the dilution refrigerator were carried out with a 30 cps ac field. Our experimental results are collected in table II. A transition above 0.3 K was detected only in $MoAs_2$ and WAs_2, which are p-type conductors belonging to the electron-rich branch of the $NbAs_2$ family. $MoAs_2$ crystals revealed a sharp transition between 0.410 and 0.415 K, whereas the transition in WAs_2 powder was smeared over 0.5K starting at 1.15K. We expect that WP_2 becomes superconducting at temperatures below 0.3 K.*

TABLE I Lattice constants of three new $NbAs_2$-type representatives.

	a (Å)	b (Å)	c (Å)	β (°)
MoGeAs	$9.13_1{}_{\pm 8}$	$3.27_7{}_{\pm 2}$	$7.65_1{}_{\pm 6}$	$118.8_6{}_{\pm 7}$
WGeAs	$9.15_7{}_{\pm 5}$	$3.28_3{}_{\pm 2}$	$7.63_8{}_{\pm 4}$	$119.1_2{}_{\pm 4}$
ReGeAs	$9.02_6{}_{\pm 4}$	$3.19_4{}_{\pm 2}$	$7.60_4{}_{\pm 3}$	$118.9_8{}_{\pm 4}$

$NbAs_2$, a representative of the group with a smaller amount of d-carriers, was tested down to 0.012 K and remained normal down to that temperature.

It therefore does seem that the d-electron-phonon interaction in these compounds is indeed small. A more detailed analysis, however, must await specific-heat measurements, from which a quantitative estimate of the d-electron-phonon interaction can be made.

TABLE II Some physical data of $NbAs_2$-type compounds T_c = transition temperature, T_n = lowest temperature down to which the compound was found to be normal; α = Seebeck coefficient near room temperature (n- or p-type). Susceptibility type at room temperature.

	T_c (K)	T_n (K)	α(μV/°K)	Susceptibility
VP_2		0.035	2 (n)	weakly paramagnetic
VAs_2		0.33	20(n)	weakly paramagnetic
NbP_2		0.3	10(n)	weakly paramagnetic
$NbAs_2$		0.012*	55(n)*	diamagnetic [2]
$NbSb_2$		0.3*	20(n)*	diamagnetic [2]
TaP_2		0.035	5(n)	weakly paramagnetic
$TaAs_2$		0.035	45(n)	diamagnetic [13]
$TaSb_2$		0.3*	12(n)*	diamagnetic [13]
MoGeAs		0.035	8(n)	diamagnetic
WGeAs		0.035	5(n)	diamagnetic
$MoAs_2$	0.41*		10(p)*	diamagnetic [14]
WP_2(r)		0.33	3(n)	diamagnetic
WAs_2	~0.9		4(p)	diamagnetic [14]
ReGeAs		0.33	25(p)	diamagnetic
$OsGe_2$		0.33		diamagnetic

*Measurements on single crystals.

Finally, since the metallic character of $MoAs_2$ and its analogues was not at all obvious from their structure, the detection of superconductivity has provided a welcome confirmation of the resistivity measurements made on powders.

References

1. S. FURUSETH and A. KJEKSHUS, *Acta Cryst.* **18** (1965) 320.
2. *Idem, Acta Chem. Scand.* **18** (1964) 1180.
3. H. G. VON SCHNERING and W. BECKMANN, *Z. anorg. Chem.* **347** (1966) 231.
4. P. JENSEN and A. KJEKSHUS, *Acta Chem. Scand.* **18** (1964) 1798.
5. B. T. MATTHIAS, T. H. GEBALLE, and V. B. COMPTON, *Revs. Mod. Phys.* **35** (1963) 1.
6. F. HULLIGER and G. W. HULL, JUN., *Solid State Comm.* **8** (1970) 1379.
7. F. HULLIGER and J. MÜLLER, *Phys. Letts.* **5** (1963) 226.
8. T. A. BITHER, C. T. PREWITT, J. L. GILLSON, P. E. BIERSTEDT, R. B. FLIPPEN, and H. S. YOUNG, *Solid State Comm.* **4** (1966) 533.

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*Unfortunately we are no longer in a position to continue these investigations, therefore, this report is somewhat incomplete.

9. N. H. VAN MAAREN, G. M. SCHAEFFER, and F. K. LOTGERING, *Phys. Letts.* **25A** (1967) 238.
10. E. BUCHER and J. L. STAUDENMANN, cited by F. Hulliger, Structure and Bonding Vol. IV (Springer-Verlag, Heidelberg 1968), Vol. IV, 83.
11. E. REVOLINSKY, G. A. SPIERING, and D. J. BEERNTSEN, *J. Phys. Chem. Solids* **26** (1965) 1029.
12. H. FRÖHLICH, *Phys. Letts.* **26A** (1968) 169; *Proc. Phys. Soc.* **Ser. 2** (1968) 544; H. FRÖHLICH and T. K. MITRA, *Proc. Phys. Soc.* **Ser. 2** (1968) 548.
13. S. FURUSETH, K. SELTE, and A. KJEKSHUS, *Acta Chem. Scand.* **19** (1965) 95.
14. P. JENSEN, A. KJEKSHUS, and T. SKANSEN, *ibid*, **20** (1966) 403.

Amended version received 27 August and accepted 22 September 1971

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Continuously Cast Aluminium–Carbon Fibre Composites and their Tensile Properties

There is a current interest in reinforcing aluminium with carbon fibres [1-3] to produce a low density composite material with high tensile strength and modulus parallel to the carbon fibre axes. Major difficulties include the lack of wetting between aluminium and the fibres and also the formation of aluminium carbide Al_4C_3 at temperatures as low as 550°C [4]. We have studied the influence of prior outgassing of the fibres and further, the use of a coating to promote wetting.

The experimental equipment [5] which was developed for the study, is shown in fig. 1. It is based on a semi-continuous casting principle: a carbon fibre tow is drawn through a long die located at the bottom of a crucible containing the aluminium melt. The liquid metal permeates the tow and solidifies in the die to produce a continuous wire. The method has the advantage of a short contact time between melt and tow and also allows an easy and rapid choice of melt temperature. The drawn wires were made from Courtaulds Grafil A or HT fibres and 99.99% pure aluminium to produce wires normally 0.5 mm in diameter and 300 mm long. Fibre content was varied between 5 and 40 vol % (fig. 2b).

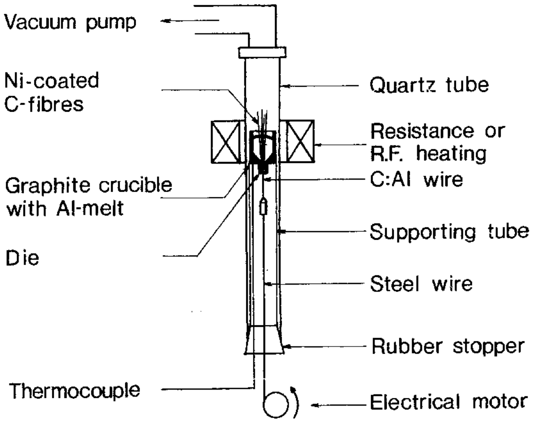

Figure 1 Wire-drawing apparatus.

A first series of carbon fibre tows was outgassed by direct Joule heating at 1000°C in a vacuum of 5×10^{-7} torr for 2 h. No wetting of these fibres was found to occur below about 1100°C. Above this temperature, wetting occurred but was accompanied and probably caused by the formation of aluminium carbide (fig. 2a) with a consequent loss of tensile properties and a concurrent proneness to decomposition in atmospheric humidity.

A second series of experiments was carried out using tows in which the fibres had been individually coated with 1 μm of nickel. The mechanical