# On the Magnetic Behavior of New 2H–NbS₂–Type Derivatives

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The magnetic behavior of compounds of the type $T_xNbS_2$ with $x = \frac{1}{3}$ and $x = \frac{1}{4}$ was studied below room temperature. No magnetic order was found with T = Ti and V, whereas with Cr the phases with $x = \frac{1}{3}$ become ferromagnetic.

Recently, van den Berg and Cossee (*1*) reported on the intercalation of Mn, Fe, Co and Ni into the layer compounds $NbS_2$ and $TaS_2$. Surprisingly, the Mn compounds revealed ferromagnetic properties whereas the remaining phases may order antiferromagnetically. Since several compounds with trivalent and tetravalent chromium ions, such as $CdCr_2Se_4$, $CuCr_2S_4$, $CrBr_3$, $CrO_2$, etc., are known to be ferromagnetic, we thought it worthwhile to study also the behavior of chromium intercalated between the layers of such compounds as $NbS_2$, $MoS_2$ or $ReS_2$. We found that incorporation of chromium into the superconductors $NbS_2$, $NbSe_2$, $TaS_2$ and $TaSe_2$ indeed leads to magnetic compounds. However, since the dependence of the magnetic properties on Cr concentration and ordering is rather complex we give here only a preliminary account on such $T_xNbX_2$ and $T_yTaX_2$ compounds (T = any $3d$ element; X = S, Se).

The host lattice of these bronze-like phases is of the 2H–NbS₂ type and consists of trigonal-prismatic anion layers with the cations and the empty octahedral holes aligned along the $c$-axis: AcA(c)BcB(c)A... (empty octahedral sites in brackets). To a certain degree the octahedral holes separating the SNbS prism layers can be occupied by cations of the same kind. In $Nb_{1+x}S_2$ $x$ may vary within $0.3 \leqslant x \leqslant 0.43$ and $0.7 \leqslant x < 1$, while in $Nb_{1+x}Se_2$ $x \leqslant 0.3$ (*3*). According to van den Berg and Cossee the phases $T_xNbS_2$ and $T_yTaS_2$ occur with $\frac{1}{3} \leqslant (x, y) \leqslant \frac{2}{3}$. At the limits ordering of the octahedrally coordinated $3d$ cations gives rise to superstructures. At these compositions one third of the available octahedral sites in each layer is either

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occupied ($x = \frac{1}{3}$) or empty ($x = \frac{2}{3}$). The ordering requires an $a = a_0\sqrt{3}$.

Our samples were prepared in powder form either by sintering pressed mixtures of $NbX_2$ or $TaX_2$ and the $3d$ element or by reacting pressed pellets of the powdered elements in evacuated silica tubes at temperatures near 1000°. Occasionally hexagonal single crystals of some millimeters grew on the surface of the pellets or at the cooler end of the quartz tube. Crystallization was enhanced by adding iodine or bromine. By such chemical transport reactions we obtained single crystal flakes up to 10 mm and 0.1–1 mm thick. The starting material was held at temperatures around 1100° and the crystals were deposited in a region which was 50–100° cooler.

Except for Cr we restricted our preparations of $T_xNbX_2$ and $T_yTaX_2$ compounds to the composition $x, y = \frac{1}{3}$, which according to the findings of van den Berg and Cossee was expected to be the lower limit of concentration. Rotation photographs of certain selenide crystals, however, led to supercells with $a = 2a_0$ which is incompatible with $x = \frac{1}{3}$. Electron beam microprobe analysis indeed revealed that in these crystals the concentration of the $3d$ element was well below this limit and close to a value $x = \frac{1}{4}$, e.g. $Cr_{0.24}Nb_{1.02}Se_2$, $Cr_{0.26}Ta_{1.05}Se_2$, $Fe_{0.26}Nb_{1.02}Se_2$, $Ni_{0.23}Nb_{1.00}Se_2$. In some Ti–Ta compounds the analysis indicated that additional Ta atoms must have been intercalated in the octahedral layers.

It is noteworthy that the very soft niobium and tantalum dichalcogenides become hard and elastic on intercalation of chromium or another $3d$ element. The greenish colour of $NbSe_2$ changes to metallic white.

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TABLE I

LATTICE CONSTANTS, MAGNETIC DATA AND THERMOELECTRIC POWER OF SOME 2H–NbS$_2$ DERIVATIVES

| Compound | $a$ (Å) | $c$ (Å) | $n_p(\mu_{Bohr})$ | $n_f(\mu_{Bohr})$ | $\theta_p$ (°K) | $a:T_N$ (°K)  $f:\theta_f$ | $\alpha_{300°K}$ ($\mu$V/°C) |
|---|---|---|---|---|---|---|---|
| Ti$_{1/3}$NbS$_2$ | 5.75$_{4\pm1}$ | 12.42$_{2\pm2}$ | 1.76 | | $-3$ | — | ~25(p) |
| V$_{1/3}$NbS$_2$ | 5.75$_{6\pm1}$ | 12.15$_{5\pm2}$ | 2.92 | | $-27$ | — | ~20(p) |
| V$_{1/3}$TaS$_2$ | 5.72$_{7\pm1}$ | 12.20$_{1\pm2}$ | 2.85 | | $-30$ | — | ~60(p) |
| Cr$_{1/3}$NbS$_2$†‡ | 5.73$_{5\pm2}$ | 12.11$_{3\pm5}$ | 3.89 | 2.9 | $+163$ | ~160$^f$ | ~50(p) |
| Cr$_{1/3}$TaS$_2$‡ | 5.72$_{0\pm2}$ | 12.12$_{8\pm4}$ | 3.78 | 3.1 | $+175$ | ~170$^f$ | ~30(p) |
| Mn$_{1/3}$NbS$_2$* | 5.782* | 12.63* | 4.82* | | $+69$* | | |
| Mn$_{1/3}$NbS$_2$†‡ | 5.78$_{2\pm2}$ | 12.59$_{8\pm4}$ | 5.16 | 3.8 | $+65$ | 48$^f$ | ~3(p) |
| Mn$_{1/3}$TaS$_2$* | — | — | 4.7* | | $+120$* | | |
| Mn$_{1/3}$TaS$_2$‡ | 5.75$_{1\pm2}$ | 12.50$_{8\pm4}$ | 4.67 | 3.9 | $+83$ | ~80$^f$ | ~1(p) |
| Fe$_{1/3}$NbS$_2$* | 5.766* | 12.21* | 4.44* | | 0* | | |
| Fe$_{1/3}$NbS$_2$†‡ | 5.76$_{8\pm2}$ | 12.20$_{0\pm5}$ | 5.55 | | $-145$ | (45$^a$?) | ~2(n) |
| Rh$_{1/3}$TaS$_2$ | 5.72$_{6\pm2}$ | 11.96$_{7\pm3}$ | | | | | |
| Ti$_{1/3}$NbSe$_2$‡ | 5.99$_{1\pm1}$ | 12.91$_{7\pm3}$ | 1.62 | | $-32$ | — | ~5(p) |
| V$_{1/3}$NbSe$_2$ | 5.99$_{7\pm2}$ | 12.68$_{6\pm2}$ | 2.94 | | $-15$ | — | ~30(p) |
| V$_{1/3}$TaSe$_2$ | 5.96$_{1\pm2}$ | 12.74$_{3\pm3}$ | 2.87 | | $-10$ | — | ~15(p) |
| Cr$_{1/3}$NbSe$_2$ | 5.98$_{1\pm2}$ | 12.67$_{6\pm4}$ | 3.98 | 3.0 | $+98$ | 105$^f$ | ~30(p) |
| Cr$_{1/3}$TaSe$_2$ | 5.95$_{4\pm1}$ | 12.70$_{0\pm3}$ | 4.12 | 3.0 | $+70$ | ~120$^f$ | ~20(p) |
| Rh$_{1/3}$NbSe$_2$ | 5.97$_{7\pm2}$ | 12.45$_{9\pm4}$ | | | | | |
| Cr$_{1/4}$NbSe$_2$†‡ | 6.87$_{8\pm3}$ | 12.58$_{3\pm5}$ | 4.62 | | $-40$ | — | ~35(p) |
| Cr$_{1/4}$TaSe$_2$†‡ | 6.87$_{0\pm3}$ | 12.63$_{8\pm5}$ | 4.77 | | $-47$ | — | ~25(p) |
| Mn$_{1/4}$NbSe$_2$‡ | 6.94$_{2\pm3}$ | 13.04$_{2\pm4}$ | 5.99 | 4.7 | $+27$ | ~25$^f$ | ~0 |
| Fe$_{1/4}$NbSe$_2$†‡ | 6.93$_{2\pm3}$ | 12.70$_{2\pm6}$ | 5.25 | | $+10$ | 175$^a$ | ~0 |
| Co$_{1/4}$NbSe$_2$ | 6.92$_{8\pm1}$ | 12.43$_{1\pm2}$ | 4.04 | | $-190$ | | ~10(n) |
| Ni$_{1/4}$NbSe$_2$†‡ | 6.91$_{1\pm1}$ | 12.42$_{1\pm3}$ | 2.62 | | $-135$ | | ~10(p) |
| Ti$_{0.38}$Ta$_{1.35}$S$_2$†‡ | 5.71$_{8\pm3}$ | 12.53$_{3\pm4}$ | Diamagnetic | | | | ~80(p) |
| Ti$_{0.22}$Ta$_{1.19}$Se$_2$†‡ | 3.44$_{3\pm2}$ | 12.87$_{9\pm5}$ | Weakly paramagnetic | | | | ~40(p) |

\* Data according to J. M. van den Berg and P. Cossee (*1*); compare also (*5*).

† Composition checked by electron beam microprobe analysis.

‡ Single crystals.

$n_f$ derived from saturation measurements (90 kOe) at 2°K.

Our experimental data are collected in Table I. All these compounds have a low, metallic resistivity and most of them show a positive Seebeck coefficient. With respect to superconductivity it might be interesting to investigate samples with much lower concentrations of the third element since with $x = \frac{1}{4}$ titanium, vanadium and even the non-magnetic rhodium completely suppress superconductivity.

The magnetic measurements revealed that in all compounds with $x = \frac{1}{3}$ the intercalated cation is trivalent whereas it appears to be divalent in the compounds with $x = \frac{1}{4}$. No magnetic ordering down to 2°K was detected in the titanium and vanadium compounds, whereas Fe$_{1/3}$NbS$_2$ and Fe$_{1/4}$NbSe$_2$ seem to be antiferromagnetic at low temperatures.

The chromium compounds with $x = \frac{1}{3}$, on the other hand, become ferromagnetic at temperatures well above liquid nitrogen. The magneton number $n_f$ in the ferromagnetic state was derived from magnetization measurements at 2°K with fields up to 90 kOe. Within the experimental accuracy (about 10 %) these values correspond well to the magnetic moment calculated from the paramagnetic susceptibility. In Cr$_{1/3}$NbS$_2$ the easy axis of magnetization lies within the hexagonal plane.

A sample of composition Cr$_{2/3}$NbS$_2$ became ferromagnetic below 65°K, while $\theta_p = -300$°K, $n_p = 3.78$ $\mu_{Bohr}$.

In Cr$_{1/3}$NbS$_2$ and its analogs the shortest Cr–Cr distance within the ferromagnetic chromium layers is $a$ and the one between the layers is $c/2$. Since these

compounds have a high electrical conductivity, magnetic coupling will take place not only via Cr–S–Cr superexchange but to a large extent via conduction electrons. The influence of the $(s, d)$ exchange may be seen from a comparison of the magnetic properties of $Cr_{1/3}NbS_2$ with those of $CrBr_3$ which also crystallizes in a layer structure and contains trivalent chromium but is a ferromagnetic insulator. The rhombohedral structure of $CrBr_3$ can be derived from that of $CdI_2$ by an ordered elimination of one third of the cations. The lattice constants of the hexagonal cell of $Cr_{2/3}Br_2$ are $a = 6.26$ Å, $c = 18.20$ Å. The distance between the cation layers is $c/3$ which is very similar to that in $Cr_{1/3}NbS_2$. Although the chromium layers contain twice as many atoms, part of which have a $\sqrt{3}$ times shorter separation, the Curie point of $CrBr_3$ is as low as 36°K which compares with that of 170°K for $Cr_{1/3}NbS_2$.

Although our crystals reveal a metallic conductivity, metallic properties of these compounds are by no means obvious, and an exact $1:3:6$ stoichiometry might modify the properties of these crystals. In the host crystals of the type $NbS_2$ the lowest $d$ subband is only half-filled whereas it is completely filled in the diamagnetic semiconductor $MoS_2$. Incorporation of additional trivalent cations $M^{3+}$ in the octahedral holes reduces the valency of niobium in $M_x^{3+}NbS_2$ and at the composition $x = \frac{1}{3}$ these compounds might contain $Nb^{3+}$ with the same electron configuration $d^2$ as molybdenum has in $MoS_2$. Nb–M interactions along the $c$-axis may account for metallic properties if these are not due to deviations from stoichiometry. Overlap of metal $d$ orbitals, however, will be extremely weak since the Cr–Nb distances are 3.03 Å and 3.17 Å in $Cr_{1/3}NbS_2$ and $Cr_{1/3}NbSe_2$, respectively, and the magnetic moments, which correspond rather well to localized $3d$ electrons of $M^{3+}$ ions, give no indication about $d$ band formation. Infinite –Nb–M–Nb–M–Nb– chains occur only if ordered identical $M^{3+}$ layers (case I) are superposed along the $c$-direction without being shifted within the hexagonal planes (i.e., if the M atoms form a primitive hexagonal sublattice, case A). If subsequent identical $M^{3+}$ layers are

shifted with respect to each other (i.e., if the M atoms are in the positions of a hexagonal or cubic close packing [cases B and C, respectively)], then only three-membered complexes Nb–M–Nb are formed, as is also true if empty layers alternate with $\frac{2}{3}$ filled layers (case II) ($\frac{1}{2}$ filled layers for $x = \frac{1}{4}$). In the cases IA, IB and IIA the $M^{3+}$ sublattice has the same periodicity in $c$-direction as the host lattice while in the other cases a larger cell is required. Though we failed to detect corresponding superstructure lines we do not think this to be conclusive. Metallic conductivity, however, would indeed plead for case IA.*

A semiconducting $Cr_{1/3}NbS_2$ with a low energy gap would be interesting for a study of the influence of the conduction electrons on the magnetic coupling (4). Even if these Cr compounds turn out to be intrinsically metallic the carrier concentration can still be varied by filling additional atoms like Sc or Nb into the empty octahedral holes or by substituting Mo for Nb.

* *Note added in proof:* According to van den Berg and Cossee (5) the ordering is of the type **IB**.

## Acknowledgments

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