Fig. 1. The R^* *versus* z curves for $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$, and $PtTe_2$.

ing uncertainties estimated from the curvature of the z,R^* curves, and the shortest interatomic distances are listed in Table 1.

Some comments on the results should be appropriate:

(i) All samples used for collecting the intensity data in this study, suffered from preferred orientation of the crystals in the glass capillaries. This effect was least significant for PtS_2 and most noteworthy for $PdTe_2$. Our first sample of $PdTe_2$, prepared at 500°C, gave $R^* = 0.52$ as the best R^* value; the second sample, heated at 300°C for four days, gave the z,R^* curve shown in Fig. 1. Within the limited accuracy the position of the minimum was the same for the two sets of intensity data. This indicates that the determinations of z in Table 1 are quite reliable despite the relatively high values of R^* shown in Fig. 1.

(ii) The only compound of this investigation having a z parameter markedly different from the ideal value $z = \frac{1}{4}$, is PtS_2. The flatness of the R^* *versus* z curve for PtS_2 explains why this deviation has not been observed by Grønvold et al.,[3] showing clearly that qualitative criteria may be insufficient for accurate structure determinations. (Because of the large difference in the X-ray scattering factors of Pt and S, R^* for PtS_2 is rather insensitive to the variations in z).

(iii) The reliability index $R^{**} = \Sigma ||\sqrt{F_o{}^2}| - |\sqrt{F_c{}^2}||/\Sigma |\sqrt{F_o{}^2}|$ can more easily than R^* be compared with the commonly used $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. In the

minima of the z, R^* curves the corresponding values of R^{**} are 0.12, 0.13, 0.083, 0.12, and 0.11 for $NiTe_2$, $PdTe_2$, PtS_2, $PtSe_2$, and $PtTe_2$, respectively. (R^{**} is 0.095 for PtS_2 at $z = 0.250$).

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On the Magnetic Properties of Niobium Selenides and Tellurides

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As part of our continued studies of niobium selenides and tellurides [1-4] we here report the results of magnetic susceptibility measurements carried out on the existing phases Nb_5Se_4, Nb_3Se_4, $Nb_{1+x}Se_2$ (0.00 ≤ x ≤ 0.29 at 25°C), "$NbSe_4$", Nb_5Te_4, Nb_3Te_4, $NbTe_2$, and $NbTe_4$.

Purity of the materials and preparation of the samples have previously been described.[1-4] The magnetic measurements were made according to the Gouy method at temperatures between 90 and 725°K and at three different maximum field strengths ($H_{max} = 4015$, 4700, and 5110 Ø, respectively). The samples were enclosed

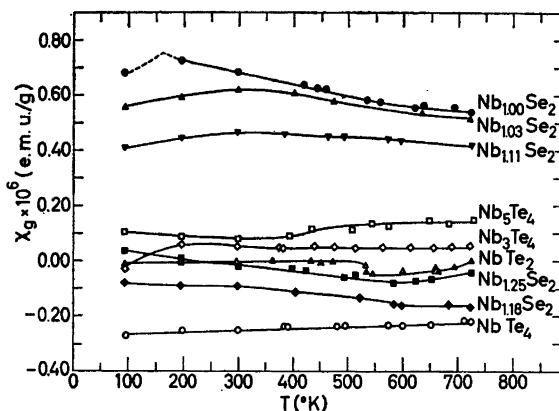*Fig. 1.* Magnetic susceptibilities of $Nb_{1.00}Se_2$, $Nb_{1.03}Se_2$, $Nb_{1.11}Se_2$, $Nb_{1.18}Se_2$, $Nb_{1.25}Se_2$, Nb_5Te_4, Nb_3Te_4, $NbTe_2$, and $NbTe_4$ as a function of temperature.

in evacuated and sealed Pyrex tubes of 3 mm internal diameter, filled to a height of about 85 mm.

Quantities, sufficient for magnetic susceptibility measurements, of the pure phases Nb_5Se_4, Nb_3Se_4, and "$NbSe_4$" were not obtained. The magnetic properties of these phases could therefore only be estimated from impure samples. However, preliminary measurements indicate weak, temperature independent paramagnetism for Nb_5Se_4 and Nb_3Se_4, whereas "$NbSe_4$" is diamagnetic.

Pure samples of the other phases were more easily prepared, and the results of the magnetic susceptibility measurements will be seen from Fig. 1. Diamagnetic susceptibility is found for $NbTe_4$, whereas $Nb_{1+x}Se_2$, Nb_5Te_4, Nb_3Te_4, and $NbTe_2$ show paramagnetic susceptibilities. (Field strength dependent susceptibilities were not observed, and mean values of the susceptibilities at the different field strengths are therefore shown in Fig. 1.)

The experimental curves in Fig. 1 have not been corrected for induced diamagnetism. The expected diamagnetism resulting from the atomic cores was calculated from the diamagnetic corrections -9×10^{-6} e.m.u. per mole Nb^{5+} (according to Klemm[5]), -47.6×10^{-6} e.m.u. per mole Se^{2-}, and -70.6×10^{-6} e.m.u. per mole Te^{2-} (according to Angus[6]). The corresponding core contributions are -0.42×10^{-6}, -0.41×10^{-6}, -0.40×10^{-6}, -0.40×10^{-6}, -0.39×10^{-6}, $-0.34 \times$ 10^{-6}, -0.39×10^{-6}, -0.43×10^{-6}, and -0.48×10^{-6} e.m.u. per gram $Nb_{1.00}Se_2$, $Nb_{1.03}Se_2$, $Nb_{1.11}Se_2$, $Nb_{1.18}Se_2$, $Nb_{1.25}Se_2$, Nb_5Te_4, Nb_3Te_4, $NbTe_2$, and $NbTe_4$, respectively. By subtracting these values from the measured susceptibilities, the total susceptibilities of localized, non-bonding electrons, valence electrons, and conduction electrons are obtained.

The correction for induced diamagnetism of $NbTe_4$ is of the same magnitude as the observed susceptibility. It is ascertained that no unpaired d-electrons are present on the niobium atoms, and a covalent type of chemical bonding may be suggested. A discussion of the observed magnetic properties and crystal structure of $NbTe_4$ in terms of the predictions of the general $(8-N)$ rule [7-9] has been given by Selte and Kjekshus.[2] Their conclusion, based on the crystallographic subcell only, is that the general $(8-N)$ rule is not satisfied for this compound. An analogous discussion for "$NbSe_4$" must await the determination of accurate composition and crystal structure of this phase.

Nb_5Te_4, Nb_3Te_4, and $NbTe_2$ show weak, almost temperature independent paramagnetic susceptibilities. Nb_5Te_4 (and Nb_5Se_4) with a crystal structure of the Ti_5Te_4 type [10] is expected to have a metallic type of bonding, and the observed paramagnetism should consequently be associated with the paramagnetism of the conduction electrons. From the crystal structure of Nb_3Te_4 (or Nb_3Se_4) and the

application of the general (8—N) rule we were expecting the magnetic susceptibility measurements of Nb_3Te_4 to give results corresponding to one unpaired d-electron per formula unit Nb_3Te_4.[4] However, the curve shown in Fig. 1 did not confirm this prediction, as Nb_3Te_4, like Nb_5Te_4, showed weak, almost temperature independent paramagnetism. Further discussion of the bonding in Nb_3Te_4 must be postponed until our planned electrical conductivity measurements have been carried out. For $NbTe_2$ no detailed discussion of the magnetic data can be made before the crystal structure is known.

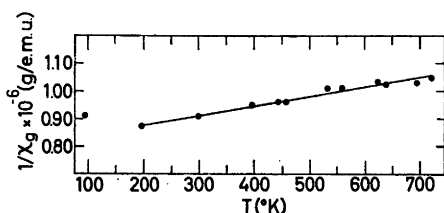The reciprocal, corrected susceptibility *versus* temperature curve in Fig. 2 shows

Fig. 2. Reciprocal magnetic susceptibility of $Nb_{1.00}Se_2$ as a function of temperature.

that the Curie-Weiss Law is almost satisfied for $Nb_{1.00}Se_2$ above room temperature with a magnetic moment of about 2.4 B.M. and a Θ-value of $-330°K$. At lower temperatures (below $\sim 200°K$) the curve indicates a transition to an antiferromagnetic state. The "spin only" approximation would demand a magnetic moment of 1.73 B.M. for one unpaired electron on the niobium atoms. The higher value observed can be accounted for by assuming a contribution from an unquenched orbital angular momentum. However, the possible inaccuracy in the diamagnetic corrections hardly justifies a detailed discussion of this discrepancy.

Addition of niobium atoms to $Nb_{1.00}Se_2$ (*i.e.* at compositions other than the niobium-poor phase limit of $Nb_{1+x}Se_2$; *cf.* Selte and Kjekshus [3]) causes a decrease in the magnitude of the observed susceptibilities and changes the Curie-Weiss Law type paramagnetism of $Nb_{1.00}Se_2$ gradually

to almost temperature independent paramagnetism (for $Nb_{1.18}Se_2$ and $Nb_{1.25}Se_2$ after correction for induced diamagnetism; see Fig. 1, where only measurements on the samples $Nb_{1.03}Se_2$, $Nb_{1.11}Se_2$, $Nb_{1.18}Se_2$, and $Nb_{1.25}Se_2$ are shown for the sake of clearness).

The magnetic properties of the $Nb_{1+x}Se_2$ phase can be discussed in terms of the general (8—N) rule: With a valence of 5 for Nb and 6 for Se the general (8—N) rule is fulfilled for $Nb_{1.00}Se_2$, assuming one unpaired d-electron on each niobium atom. $Nb_{1.00}Se_2$ can thus be described as a normal valence compound in accordance with the observed crystal structure (Selte and Kjekshus [3]) and predicted to be a semiconductor. Addition of niobium atoms gives rise to gradually filling of the conduction band and simultaneously a delocalization of the unpaired electrons. (Similar observations are made for the $Ta_{1+x}Se_2$ phase by Bjerkelund and Kjekshus.[11])

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