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The Low-Temperature Electrical and Magnetic Properties of $TaSe_2$ and $NbSe_2$†

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$NbSe_2$ has been reported to have an anomalous sign change in the Hall coefficient at low temperatures. In this paper it will be shown that the sign change is associated with a magnetic ordering. In addition, electrical and magnetic studies have been carried out on $TaSe_2$, and a similar anomalous sign change is observed in the Hall coefficient at about 90°K. A small degree of magnetic ordering is also present in this compound near the temperature at which the Hall coefficient begins the rapid change from *p*- to *n*-type.

Introduction

In a previous paper (*1*) the resistivity (ρ) and Hall coefficient (R_H) of $NbSe_2$ were reported from about 350°K down to its superconducting transition temperature (T_c) of 7°K. These results are shown in Fig. 1. The Hall voltage is almost constant and positive above 60°K, but the Seebeck coefficient is negative. The magnitude of the Hall coefficient starts to drop below 60°K and changes sign at about 26°K. The magnetic susceptibility (χ_g) of $NbSe_2$ has been reported by Selte and Kjekshus. (*2*) From their data they concluded that $NbSe_2$ became antiferromagnetic between 100° and 200°K. We have determined the magnetic susceptibility using a Faraday balance and we do not find a Néel point in that temperature range. Examination of their data indicated that their conclusion was based on an insufficient number of measurements below 200°K.

$TaSe_2$ has the same hexagonal layered structure as $NbSe_2$, and also exists in a number of polymorphic forms (*3–5*) depending on the stacking sequence of the trigonal prismatic SeTaSe slabs. For the two-layer polymorphic form of $TaSe_2$, the Ta atoms line

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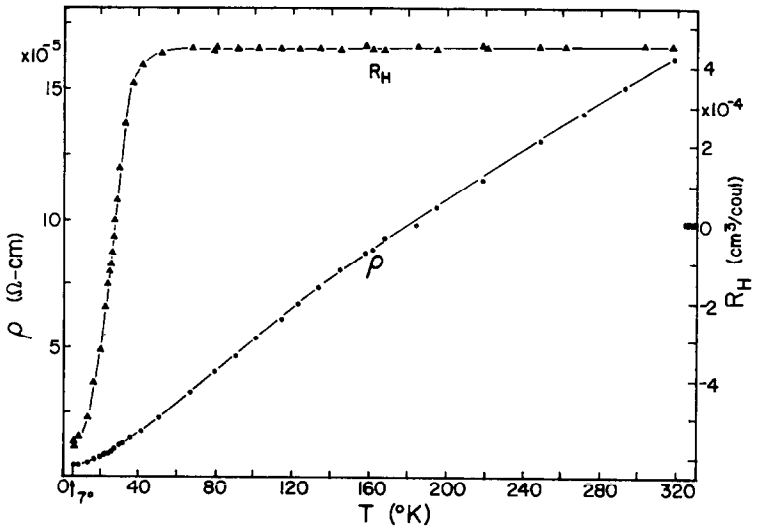

FIG. 1. The resistivity and Hall coefficient of $NbSe_2$ as a function of temperature.

up in the c direction similar to the Nb atoms in two-layer form of $NbSe_2$. $TaSe_2$ is also superconducting, with a T_c between 0.13 and 0.15°K for the two-layer form (*6*). Kadijk, Huisman and Jellinek (*3*) reported that the two-layer $TaSe_2$ is formed between 900° and 1200°. A more recent paper by Huisman and Jellinek (*5*) showed the two-layer polymorph is formed when the sample is annealed at 600° and then slow-cooled.

Quinn *et al.* (*7*) have made magnetic susceptibility measurements on the various compositions of $TaSe_{2\pm\delta}(TaSe_{1.85} - TaSe_{2.07})$. They reported peaks in the susceptibility curves for all compositions, and the temperatures at which the peaks occur vary from 110°K to 130°K. To date, there have been no electrical resistivity and Hall measurements reported on $TaSe_2$. The purpose of this paper is to report the magnetic measurements on $NbSe_2$ and the electrical and magnetic measurements on $TaSe_2$. In addition, the influence of the magnetic properties on the electrical properties of these compounds will be discussed.

Experimental

$NbSe_2$ powder and single crystals were prepared in the same manner as described in Ref. 1. Similarly, $TaSe_2$ was prepared by heating stoichiometric amounts of the elements in an evacuated silica tube at 600° for four days. Single crystals of $TaSe_2$ were grown by chemical vapor transport using iodine as the transporting agent (*8*). The charge zone and growth zone temperatures were 725° and 675° respectively. The crystals were washed in carbon tetrachloride and acetone and then were sealed in an evacuated silica tube for annealing. They were annealed at 600° for two days before slow cooling to room temperature at about 10°/hr. The $TaSe_2$ crystals obtained were in the form of thin platelets (0.002–0.020 cm) with mirror-like surfaces perpendicular to the crystallographic c direction, similar to the $NbSe_2$ crystals. Some of the crystals were larger than 5×10 mm.

The stoichiometry of $TaSe_2$ was determined by oxidizing the crystals at 720° in an atmosphere of oxygen to Ta_2O_5, while monitoring the weight change with a Cahn electrobalance. The samples used in these measurements had a stoichiometry of $TaSe_{1.995\pm.005}$. The crystals were also X-rayed by the single crystal precession technique, and only the two-layer polymorphic form was found.

The resistivity and Hall measurements were made in the same manner as described in Ref. 1. Magnetic measurements were made on ground-up single crystals using a Faraday balance (*9*) and the results were corrected for ferromagnetic impurities using the Honda–Owen method (*9*, *10*).

Results

Figure 2 shows the magnetic susceptibility of $NbSe_2$ as a function of temperature. Below 60°K, χ_g starts to increase and peaks at about 40°K. Above 100°K, the curve agrees well with the results reported by Selte and Kjekshus (*2*), but the peak they postulated between 100 and 200°K is not present.

Figure 3 shows the resistivity versus temperature curve for $TaSe_2$. The lowest temperature reached was about 4°K. We did not attempt to check T_c, which

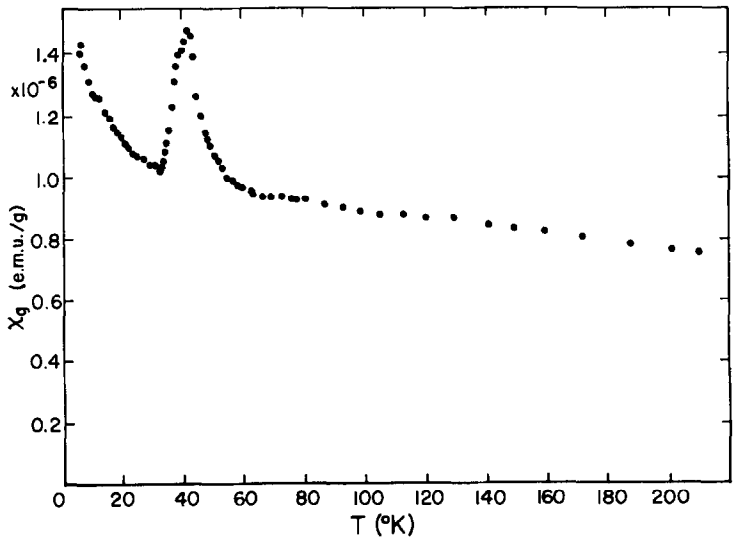

FIG. 2. The magnetic susceptibility vs. temperature for $NbSe_2$.

has been reported to be beween 0.13° and 0.15°K (*6*) for this compound. There is a sharp break in the resistivity curve at 110°K. The break varies by only ±1°K from sample to sample. Above 110°K, the slope of the resistivity curve is constant.

Figure 4 shows the Hall coefficient of $TaSe_2$ as a function of temperature. Above 120°K, R_H is positive and almost temperature independent, but below 120°K the magnitude of R_H starts to decrease. The Hall coefficient changes sign at 90°K (±3°K from sample to sample). Below about 35°K, the magnitude of R_H decreases toward zero again.

Figure 5 shows the magnetic susceptibility vers temperature curve for $TaSe_2$. The peak is at abo 110°K, but is much less distinct than the peak $NbSe_2$.

Quinn *et al.* (*7*) have also done magnetic su ceptibility measurements on $TaSe_{2\pm\delta}$, and th found peaks for all compositions in the temperatu range of 110°K to 130°K. The magnitude of χ_g fro our data agrees with the curve they reported for t nearest composition ($TaSe_{2.02}$) except that t maximum in their curve appears between 120° a 130°K, compared to 110°K in our measuremen

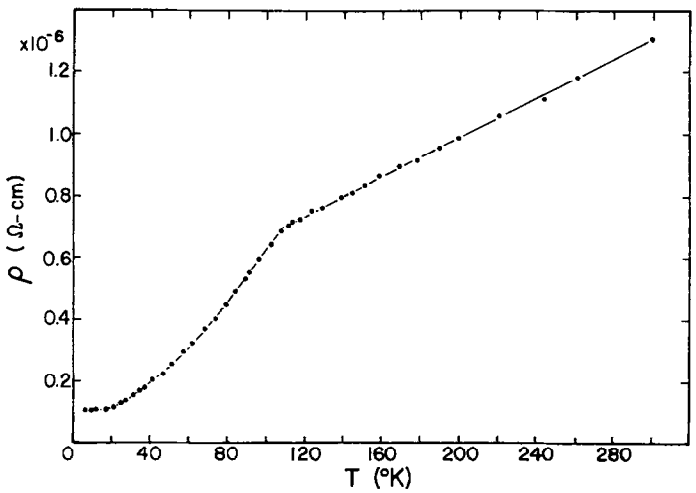

FIG. 3. The resistivity vs. temperature for $TaSe_2$.

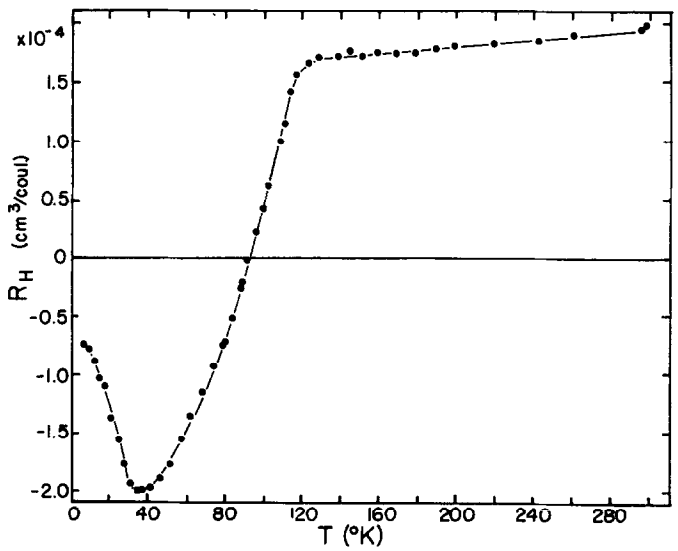

FIG. 4. The Hall coefficient vs. temperature for $TaSe_2$.

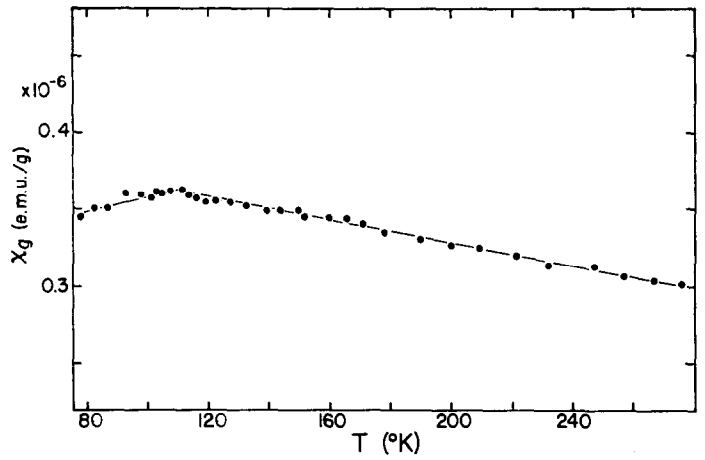

FIG. 5. The magnetic susceptibility vs. temperature for $TaSe_2$.

The difference is probably due to the difference in composition as well as differences in the preparation and annealing of the samples.

Discussion

As mentioned in Ref. 1, the most interesting phenomena observed are the relatively rapid transition of R_H from *p*-type to *n*-type as the temperature is lowered and the fact that the signs of the Hall coefficient (positive) and Seebeck coefficient (negative) at room temperature are opposite. The difference in sign between the Hall and Seebeck coefficients can usually be explained by assuming the presence of two types of carriers (*11*, *12*) having a mobility ratio much greater or much less than one, since R_H has a squared dependence on the mobilities of the carriers, while the Seebeck coefficient has only a linear dependence. The change of sign of the Hall coefficient can usually be justified if the numbers of electrons or holes and/or the mobilities of the electrons or holes vary with temperature. Hall mobilities have been calculated for the range of temperatures where the Hall coefficient is almost constant for both compounds, assuming only one type of carrier is present, and there is no indication that the mobility is changing rapidly with temperature. Also, from Goodenough's band scheme (*13*) (discussed in Ref. 1) for these compounds, the metallic behavior arises from a half-filled band, and the number of carriers should be constant, as is borne out by R_H. Therefore, the conventional way of explaining the sign change in the Hall coefficient as being the temperature dependence of either the numbers or mobilities of the carriers is not consistent with the observed data. This is also indicated in the resistivity curve for $TaSe_2$, where the break is very sharp. Since the peaks in the magnetic susceptibility curves for both compounds occur at a temperature where the Hall coefficient is changing, the magnetic ordering may be responsible for the anomalous sign change.

Similar behavior has been observed in NiO (*14*) and α-Fe_2O_3, (*15*) which are semiconducting rather than metallic. In NiO the Hall coefficient changes sign in the vicinity of the Néel point. Above this temperature the Seebeck coefficient is positive as expected, but the Hall coefficient is negative. For α-Fe_2O_3 a sign change in the Hall coefficient has also been observed. In the high temperature paramagnetic region the Hall coefficient is positive, but the Seebeck coefficient is negative. However, in the low temperature antiferromagnetic region both Hall and Seebeck coefficients are negative. Thus both NiO and α-Fe_2O_3 have anomalous signs for the Hall coefficient in the paramagnetic region.

Except for being metallic, the behavior for $NbSe_2$ and $TaSe_2$ closely resembles that of the anomalous Hall coefficients found in some of these antiferromagnetically ordered semiconductors. Although it is not possible to determine unambiguously the nature of the magnetic ordering, both $NbSe_2$ and $TaSe_2$ could be considered to be antiferromagnetic from consideration of the shape of the magnetic susceptibility curves. However, the magnitude of the susceptibility is smaller than that usually observed for antiferromagnetic materials. The maxima in the susceptibility curves occur at 40°K for $NbSe_2$ and 110°K for $TaSe_2$. The peaks in the susceptibilities suggest that the anomalous signs of the Hall coefficient may be closely related to the magnetic ordering present in these compounds. Maranzana (*16*) has recently attempted to explain the anomalous Hall coefficient in antiferromagnetic compounds like NiO and α-Fe_2O_3. He showed that an extra-

ordinary Hall effect exists in the paramagnetic region which is subtracted from the ordinary Hall effect.

In $NbSe_2$ and $TaSe_2$, if the magnetic moment, which arises from the magnetic ordering shown in the magnetic susceptibility curve, interacts with the mobile electrons in the e^T level, then an anomalous Hall coefficient similar to that of NiO and α-Fe_2O_3 can exist.

In $TaSe_2$, there is a sharp break in the slope of the resistivity versus temperature curve at 110°K. This change of slope can be caused by a change in the scattering mechanism. If there is a magnetic ordering, the ordered spins no longer scatter the electrons, and an increase in the mobility of the electrons results. Therefore, the resistivity decreases giving rise to an increase in the slope of the resistivity curve. In the Hall measurement, the magnitude of the Hall coefficient starts to drop sharply below 110°K, the temperature at which the break in the slope of the resistivity curve occurs.

Above 40°K, the shape of the Hall coefficient versus temperature curve for $TaSe_2$ is very similar to that of the $NbSe_2$, but the transition occurs at a much higher temperature. Since this transition temperature is above the liquid nitrogen temperature, it is possible to determine whether or not this transition is due to a crystallographic change. A sample of $TaSe_2$ was X-rayed at liquid nitrogen temperature, but there was no apparent crystallographic transformation. Thus it is believed that the sign change in the Hall coefficient in $TaSe_2$ and probably in $NbSe_2$ as well is not a result of a crystallographic change.

Below 40°K the Hall coefficient of $TaSe_2$ decreases in magnitude again. Without further studies on $TaSe_2$ it is not clear what causes this decrease. It has been reported (*17*) that there is a peak in the Hall coefficient at around 40°K for metals like Cu, Ag, and Au. This peak in the Hall coefficient in $TaSe_2$ may be similar to the effect observed in these noble metals.

Although there is no apparent break in the resistivity curve for $NbSe_2$, it is possible that the break could be masked by the rapid change of the slope of the resistivity curve at the temperature where the break would be expected. Thus a change in the scattering mechanism due to magnetic ordering might not show in the resistivity curve.

Conclusion

This study on the transport properties of the layer-type compounds of the Groups VB and VIB dichalcogenides represents a first step towards understanding their behavior. With the present available data on two of the metallic compounds in this group, it appears that the transport properties of these compounds are stongly influenced by their magnetic properties. At high temperatures, the disordering of the magnetic spin may give rise to anomalous Hall voltages similar to the effects observed in the paramagnetic states of NiO and α-Fe_2O_3. The theory explaining the anomalous Hall effect in magnetically ordered materials is not well established, and there remains much to be done in the theoretical interpretation of the anomalous Hall effect in antiferromagnetic materials, both metallic and semiconducting.

The band picture as proposed by Goodenough predicted the metallic properties of the compounds, but the model was not extended to give the explicit behavior of the charge carriers. On the whole, $NbSe_2$ and $TaSe_2$ behave similarly, in that both compounds are metallic and superconducting, and the Hall measurements for $TaSe_2$ above 40°K are very similar to the Hall measurements of $NbSe_2$.

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