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Magnetic, Electrical and Crystallographic Study of the Magnetic Transitions in NiAs-Type Crystals

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1. Introduction

Magnetic and electrical properties of 3d-transition metal chalcogenides with the NiAs-type structure cover a very wide spectrum. For example, MnTe and NiS are antiferromagnetic, while CrTe is ferromagnetic. Furthermore, MnTe and CrTe show semiconductive (or semimetallic) and metallic electrical behaviors, respectively. This variety of the physical properties is thought to be owing to the presence of 3d-levels situated near the valence bands in these crystals. It is of interest to study the exchange cooperative properties in NiAs-type compounds in order to consider the electronic characters of d-electrons in solids. In part I, magnetic structures, magnetic transitions and electrical properties of NiAs-type compounds are briefly reviewed on the basis of the molecular field theory.

2. Antiferromagnetism in MnTe⁽¹⁾⁻⁽⁴⁾

The symmetry of crystalline field at the position of Mn atoms induced by six Te atoms in MnTe is nearly cubic, since (c/a) is very close to 1.63. From this simplicity, MnTe is selected as the starting specimen in the series of these works. It has been carefully prepared to be free from MnTe₂ and MnO, because the magnetic and electrical properties of MnTe are much influenced by a small amount of contamination of MnTe₂.

The magnetic structure of MnTe consists of ferromagnetic sheets in *c*-planes which are coupled antiferromagnetically along the *c*-axis. The direction of spins lies within the ferromagnetic sheets. The magnetic form factor obtained by Hastings *et al.* for MnO, MnS, MnS₂, MnSe₂ and MnTe₂, and the present experimental result are similar to each other. Then the distribution of unpaired electrons is almost spherical but slightly expanded from that of the free Mn⁺⁺ ion calculated by Freeman and Watson.

The number of unpaired electrons on Mn atoms has been separately obtained from neutron diffraction measurements, and from the magnetic susceptibility data by using the Curie-Weiss law. The value 4.7 obtained from the former method is considerably smaller than 5.1 which is obtained from the latter one. The latter value is refined to be 4.8 when the derivatives of the exchange integrals relating to interaction distances are introduced into the Curie-Weiss law. Therefore, the intrinsic number of the unpaired electrons localized on Mn atoms is the value of 4.7, which is considerably smaller than that predicted from the Hund rule for the

free Mn^{++} ion. Such a result of exchange analysis is also fairly established in the case of CrTe showing the similar discrepancy.

The Néel temperature, T_N has been determined to be 307°K by observing the temperature-dependence of the intensities of magnetically scattered neutrons. Hydrostatic compressions and Se-substitution for Te have been used as the methods to decrease the interaction-distances in MnTe. The Néel temperature increases linearly at a rate of $dT_N/dP = +2.6$ degree/kbar at pressures up to 10 kbar, while it hardly shifts with increase of substituted amounts of Se. This inconsistency in the decreasing effect of interaction-distances on the Néel temperature is thought to be due to the effect of a certain indirect exchange interaction through the chalcogenide atoms.

3. Magnetic and Crystallographic Properties of NiAs-Type Vanadium Chalcogenides⁽⁵⁾

Axial ratio, (c/a) in VSe is nearly 1.63, which implies that the V atoms lie in the nearly cubic crystalline field produced by the Se ions. The (c/a) of sulfide and telluride are, respectively, larger and smaller than 1.63. Therefore, the V ions lie in the trigonally distorted field. It is considered that the effect of distorted field on the magnetic properties can be clarified by investigating these compounds, if the magnetic structures and the magnetic form factors are determined. In the part III magnetic and crystallographic properties of these compounds have been studied by means of x-ray and neutron diffraction and magnetic susceptibility measurements.

Vanadium sulfide has the normal NiAs-type structure in the composition range from $\text{Vo}_{.47}\text{So}_{.53}$ to $\text{Vo}_{.48}\text{So}_{.52}$. The phase with the composition of $\text{Vo}_{.46}\text{So}_{.54}$ has a NiAs-like structure including a partially ordered arrangement of vanadium vacancies. The susceptibility-temperature curve for the former phase shows an breaking point at about 1000°K similar to that arising from an antiferromagnetic transition. The neutron and x-ray diffraction analysis for $\text{Vo}_{.47}\text{So}_{.53}$ has been disclosed that the anomaly is attributable neither to crystallographic nor to magnetic transformations.

The Curie-Weiss law with the asymptotic Curie temperature, $T_p = -2896^\circ\text{K}$, and the effective number of Bohr magneton, $P_{eff} = 4.6 \mu_B$ fits the magnetic susceptibility observed at temperatures above 480°K . Below the critical temperature, it deviates from the Curie-Weiss law. The neutron diffraction pattern taken at 150°K detects no localized magnetic moment larger than one-fifth of the value estimated from the observed effective number of Bohr magneton. The anomalous magnetic behaviors could not be explained by a simple ionic model.

Vanadium telluride crystallizes in the NiAs-type structure at the narrow range around the composition of V_6Te_7 . Its susceptibility observed above 77°K is de-

scribed by the Curie-Weiss law with $P_{eff}=3.98\mu_B$ per vanadium atom. This value is in good agreement with that expected for the $^4F_{3/2}$ state.

4. Magnetic Transitions in NiAs-Type Sulfides⁽⁶⁾⁻⁽⁸⁾

A number of the interesting magnetic transitions which are different from the second order and magnetically order-disorder transition, have been reported on the NiAs-type sulfides. The magneto-elastic phenomena accompanying these transitions are investigated in part IV in order to study the behaviors of exchange integrals upon the variation of interaction-distances.

The temperature-dependence of lattice parameters has been measured by low temperature x-ray diffraction method in $\text{CrS}_{1.17}$ having an ordered structure of chromium vacancies. A large amount of non-phonon contributions are detected on the thermal expansion of a - and c -axes below the ferromagnetic Curie temperature, $T_c=310^\circ\text{K}$. They are proportional to the square of order-parameter, and change with the thermal variation of helicomagnetic turn-angle in the antiferromagnetic phase below the transition temperature, $T_t=164^\circ\text{K}$. The distance-derivatives of exchange integrals are tentatively evaluated from these exchange-striction data.

The change in spin-direction and crystal-symmetry has been reported by previous workers at the temperature, T_a about 410°K in FeS. The effect of pressure on the kink in temperature-dependence of electrical resistivity at T_a has been investigated at hydrostatic pressures up to 11 kbar. The transition temperature shifts linearly with the rate of $dT_a/dP=-0.8$ degree/kbar. The observed rate is in nearly agreement with that calculated from the Clausius-Clapeyron relation for the first-order transition.

The temperature-dependence of electrical resistivity in NiS has been investigated in the vicinity of the first-order antiferromagnetic transition temperatures at hydrostatic pressures up to 7 kbar. The transition has characteristics of semiconductive- or semimetallic-to-metallic transition. The transition point, T_r is observed at 230°K at atmospheric pressure. It is lowered as the pressure is increased with the rate $dT_r/dP=-6$ degree/kbar. The transition can be described in terms of the electronic rearrangement in d -orbitals of nickel atoms between localized and collective electronic states.

5. Discussions⁽⁴⁾

The numbers of unpaired electrons in NiAs-type crystals have been obtained from paramagnetic susceptibilities through the Curie-Weiss law. They are in very nearly agreement with those calculated for the ions having high-spin or low-spin states, usually observed for oxides and complex salts. This result was regarded as an evidence of the predominance of ionic bonding in the NiAs-type compounds.

On the other hand, the value obtained from the direct methods, *i.e.*, neutron diffraction and saturation and saturation magnetization measurements, are observed to be smaller than those values. The discrepancy has been frequently found in NiAs-type compounds. The experimental results in this study reveals that the magnetic cooperative phenomena in NiAs-type compounds are remarkably affected by the distance-dependent exchange interactions. The former values can be nearly agreed with the latter, when the terms of the distance-derivatives of exchange integrals are inserted into the Curie-Weiss law.

The values of electrical resistivity of NiAs-type compounds distributes in the range of 10^{-1} to 10^{-5} ohm-cm. An empirical correlation between the electrical data and the carrier concentrations has been investigated in part II and V. The first and the second Jones zones for the NiAs-type crystals are constructed from the (101), and the (102) and its equivalent planes, respectively. The electrons to be filled into these zones are evaluated from the sum of the numbers of the outer shell *s* and *p* electrons and the *d*-electron-deficiency, Δ . The quantity, Δ is defined by the relation:

$$\Delta = (\text{number of the unpaired electrons predicted from the Hund rule}) \\ - (\text{observed intrinsic value of unpaired electrons}).$$

A correlation is found to hold between the conductivities and the filled numbers of electrons in the Jones zones.

Consequently, it is proposed that the NiAs-type compound has semimetallic or metallic nature with narrow conduction bands partially including *d*-electrons.

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