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学位論文題目	The Néel Temperature and Magnetovolume Effects in γ-MnRh Alloys （γ-MnRh 合金のネール温度と磁気体積効果）
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論文内容要旨

γ-Mn alloys and compounds have been extensively studied from viewpoints of both practical applications and fundamental studies. For applications, γ-Mn alloys and compounds having a high Néel temperature are considered as promising materials for antiferromagnets of spin-valve layers. The antiferromagnet in the spin-valve layers plays an important role to pin the spin alignment in the neighboring ferromagnetic layer. Therefore, it is desirable to investigate the antiferromagnets having strong exchange interaction, or a high Néel temperature. Moreover, the thermal expansion property and crystal structure should be investigated from the point of thermal stability of the characteristics of the spin-valve layers. However, information on physical properties of antiferromagnetic γ-Mn alloys is not enough. For fundamental studies, on the other hand, γ-Mn alloys and compounds are considered as the intermediate materials between localized electron systems and itinerant electron systems in the unified theory which takes into account spin fluctuations. The magnetic properties of γ-Mn alloys and compounds have been discussed by the localized electron model so far. If γ-Mn alloys have itinerancy, the itinerant *d* electrons affect their physical properties. However, even in the unified theory mentioned above, the quantitative explanation of the magnetic properties is restricted to nearly ferromagnetic, weakly ferromagnetic and antiferromagnetic materials. The quantitative explanations for the intermediate materials having both localized and itinerant characters are not so easy. Consequently, detailed experimental and theoretical investigations on fundamental physical properties for such materials are highly required.

The main motivation of the present study is to investigate the various physical properties of γ-MnRh alloys and discuss them in terms of the itinerant electron model. The transmission electron microscope and X-ray powder diffraction measurements were carried out in order to make clear the existence region of the ordered and the disordered phases, and their crystal structures. The magnetic measurement was made to investigate the concentration dependence of the Néel temperature and the magnetic properties. On the basis of these results, the difference between the Néel temperature among the substitutional elements is discussed from the viewpoints of the band theory. In order to investigate the thermal expansion coefficient and the Debye temperature, the thermal expansion and the low-temperature specific heat measurements were carried out. The magnetic contribution to the thermal expansion was also discussed by using these results. The electrical resistivity and X-ray powder diffraction measurements under high pressures were also carried out to investigate the pressure effects on the Néel temperature and the compressibility. Finally, the phase diagram of Mn-Rh disordered alloys below the Néel temperature was demonstrated, and the relation between the crystal structure and the structure of SDW (spin density wave) was discussed.

In Chapter 1, the magnetic properties of Mn and Mn system alloys and compounds, the spin-valve layers, background of the magnetic studies on γ-MnRh and related alloys and objective of the thesis were briefly surveyed.

In Chapter 2, the sample preparation method and the experimental procedures of transmission electron microscope, X-ray powder diffraction, magnetic, thermal expansion, low-temperature specific heat and electrical resistivity measurements were described. Moreover, the electrical resistivity and X-ray powder diffraction measurements under high pressures were also explained.

In Chapter 3, the experimental results were analyzed. Various data such as the crystal structure, order-parameter of the ordered alloys, concentration dependences of the lattice constant and the Néel temperature, thermal expansion characteristics, Debye temperature, electrical specific heat coefficient, electrical characteristics, pressure dependence of the Néel temperature and the compressibility of γ-MnRh alloys were discussed.

In Chapter 4, the magnetic properties of γ-MnRh ordered and disordered alloys were discussed in the following four sections.

In Section 4-1, the difference between the Néel temperature depending on the substitutional elements was discussed. Figure 1 shows the concentration dependence of the Néel temperature T_N of γ-MnRh ordered and disordered alloys. The solid and open circles respectively stand for T_N of the ordered and the disordered alloys. As seen in the figure, T_N of the ordered alloys is 160~200 K higher than that of the disordered alloys, and T_N converges to that of pure γ-Mn. In comparison with other γ-Mn alloy systems, it is clarified that γ-MnRh has a very high T_N next to that of γ-MnIr ordered alloys. The difference between T_N due to the substitutional elements was discussed by the *d* electron number, which is associated with the exchange constant calculated by the multiple scattering theory as a function of the Fermi energy. It is suggested that T_N of γ-Mn alloy systems becomes higher as the valence electron number in the substitutional element becomes smaller.

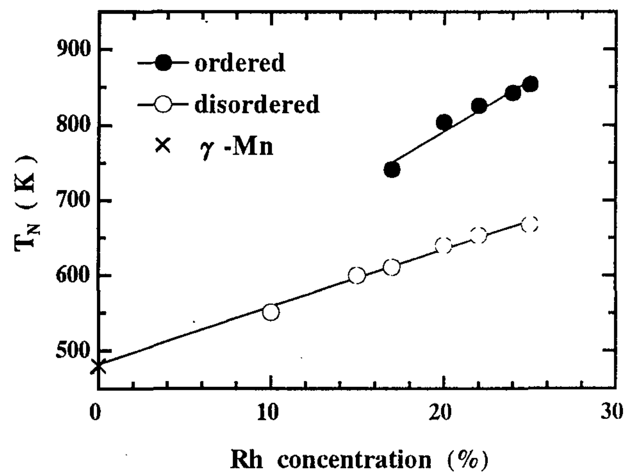

Fig. 1 Concentration dependence of the Néel temperature T_N of γ-MnRh ordered and disordered alloys.

In Section 4-2, the magnetic contribution to the thermal expansion coefficient in the paramagnetic region for γ-MnRh ordered alloys was discussed. Figure 2 shows the temperature dependence of the thermal expansion coefficient of $Mn_{75}Rh_{25}$ ordered alloy. The solid line stands for the sum of the phonon and electrical contribution calculated by the Grüneisen relation using the low-temperature specific heat data. The Debye temperature and the electrical specific heat coefficient were estimated to be 363 K and 3.9 mJ/mol-K^2, respectively. The observed thermal expansion coefficient in the paramagnetic region is about 30× 10^{-6}/K, and 10×10^{-6}/K larger than the calculated value. Such a large thermal expansion coefficient of γ-MnRh ordered alloy cannot be explained by the sum of the phonon and the electrical terms but by the large magnetic contribution which is characteristics in itinerant electron magnets.

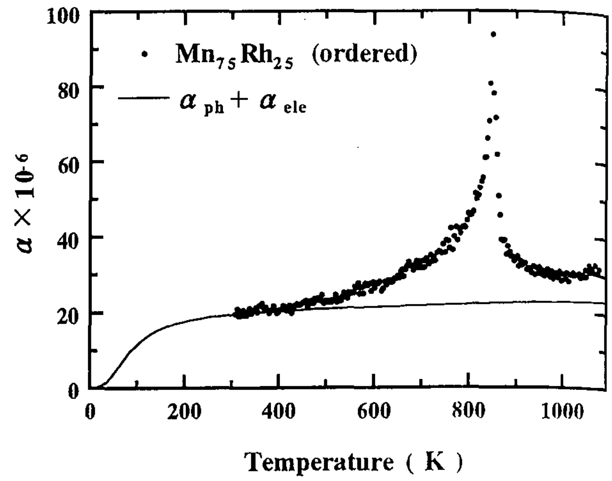

Fig. 2 Temperature dependence of the thermal expansion coefficient of $Mn_{75}Rh_{25}$ ordered alloy.

In Section 4-3, the pressure dependence of the Néel temperature of γ-MnRh ordered alloys was discussed thermodynamically by using the thermal expansion data and in terms of the band theory. From the thermal expansion data of γ-MnRh ordered alloy, a negative magnetovolume effect was observed and the sign at the peak for the thermal expansion coefficient is positive as shown in Fig. 2. Actually, the pressure dependence of the Néel temperature of $Mn_{75}Rh_{25}$ ordered alloy is given to about 7.0 K/GPa from electrical resistivity data under high pressures. These results are consistent with the thermodynamical relation. Moreover, the pressure dependence of the Néel temperature was discussed qualitatively by using the compressibility data of about 1.4×10^{-2}/GPa. In the SSF (Single-site Spin Fluctuation) theory, the Curie and the Néel temperature T_N are expressed as a function of the band width and the electron-electron interaction U, and volume dependence of the electron-electron interaction μ defined as dlnU/dlnV. In the present study for $Mn_{75}Rh_{25}$ ordered alloy having a negative magnetovolume effect in the thermal expansion curve, μ is estimated to be about –2.75. In the case of antiferromagnetic materials, dT_N/dP becomes negative when the value of μ is less than –10/3. The sign of the dT_N/dP depends on the value of μ, therefore, it is concluded that the volume dependence of the electron-electron interaction μ plays an important role in the magneto-volume effects in γ-MnRh alloy under pressures.

In Section 4-4, the relation between the magnetic structure and the lattice distortion for γ-MnRh disordered state was discussed. From X-ray powder diffraction data, the following crystal structures were observed in γ-MnRh disordered alloys; face-centered-cubic (fcc), -tetragonal (fct) and -orthorhombic (fco) crystal structures. Additional anomaly was observed below the Néel temperature in the temperature dependence of the magnetic susceptibility of γ-MnRh disordered alloys below 15 % Rh. This behavior is considered to correspond to the phase transition. From the observed data, the

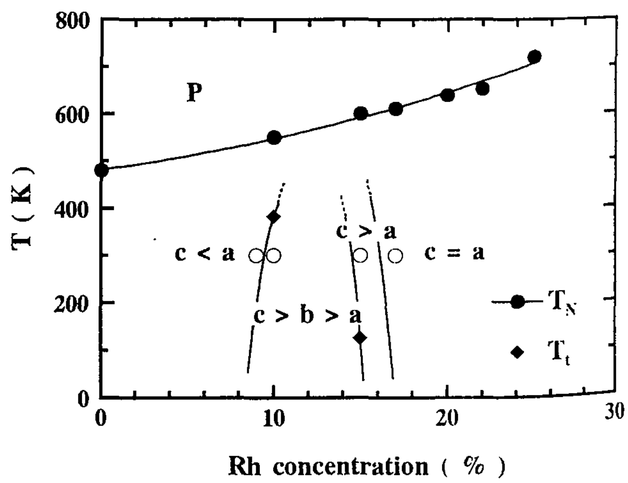

Fig. 3 Phase diagram of Mn-Rh disordered alloy.

phase diagram of Mn-based Mn-Rh disordered alloy is given in Fig. 3. In the figure, the solid circles stand for the Néel temperature and the solid squares indicate the phase transition temperature decided from the magnetic data. The open circles indicate the experimental temperature of X-ray powder diffraction. It has been pointed out that there is a close correlation between the structure of SDW (spin density wave) and the crystal structure in Mn-based Mn alloy systems. Comparing between the observed magnetic data and the theoretical investigations, the magnitude of the magnetic susceptibility at zero temperature is different among the three configurations, it is suggested that the lattice distortion of Mn-Rh disordered alloys is strongly correlated with the structure of SDW. Consequently, the formation of the S (single)-SDW phase coincides with a tetragonal lattice distortion with $c < a$, the D (double)-SDW phase with $c > a$ and the T (triple)-SDW with a cubic symmetry which results in a uniform volume contraction with $a = c$.

In Chapter 5, the present results and the discussion were concluded, and the main results were summarized.

審査結果の要旨

ハードディスクの磁気ヘッドに使われるスピンバルブ膜において反強磁性合金が始めて実用材料として使われるようになり、γ-Mn 系合金が有望な物質として着目されている。ところが、状態図を含めこれらの物質の基礎物性に関するデータが不足しているため、反強磁性合金に関する基礎研究が切望されている。一方、理論的な観点から γ-Mn 系合金は局在モーメント系と遍歴電子系との中間物質と見なされ、様々な物理的性質に対してバンド理論による解釈の必要性が提起されている。著者は熱処理の違いによって規則相と不規則相の両方を示す反強磁性体 γ-MnRh 合金に着目して様々な基礎物性を調べてバンド理論の立場から考察した。本論文はこれらの成果をまとめたもので、全文5章より成る。

第1章は序論であり、本論文の背景及び目的を述べている。

第2章では実験方法として試料の作製方法、構造解析、磁化測定、熱膨張測定、比熱測定、電気抵抗測定、圧力中物性測定法について説明している。

第3章では実験結果と解析法について述べている。γ-MnRh 合金のネール温度の組成依存性をはじめ、伝導特性、熱膨張特性、デバイ温度、ネール温度の圧力依存性、圧縮率などの結果が示されている。

第4章では考察として、以下の4つの項目について議論している。

1. γ-Mn 系合金のネール温度が添加元素の種類によって異なる点に着目し、バンド計算と多重散乱理論の結果を基に Mn サイトの $3d$ 電子数を考慮することでネール温度の違いを説明できることを指摘した。この結果はさらに高いネール温度を示す物質を探索する上で非常に意味深い結果である。
2. γ-MnRh 規則相合金の熱膨張係数が常磁性領域において非常に大きな値を示すことに着目し、その原因が磁気的寄与によることを明らかにした。この結果は γ-MnRh 合金が遍歴的性質を示すことを示唆する重要な結果である。
3. γ-MnRh 規則相合金のネール温度の圧力依存性についてバンド理論で考察し、この合金を含めた反強磁性体の圧力中における物性は電子間クーロン相互作用の体積変化率が非常に重要な因子であることを明らかにした。このように高いネール温度を示す物質、特に反強磁性体でネール温度の圧力依存性や圧縮率が測定された例は非常に少なく、貴重な結果である。
4. Mn-Rh 不規則相合金の結晶歪みと磁気構造との関連性に着目し、磁化率の温度依存性で観測される異常が結晶構造の変化だけでなく磁気構造の変化も伴っていることを示した。γ-Mn 系合金の磁化率の振舞いをこのように定量的に考察した例はなく、また、Mn-Rh 不規則相合金のネール温度以下における相図は始めての報告である。

第5章は総括および結論である。

以上要するに本論文は、スピンバルブ膜の反強磁性体として有望な γ-MnRh 規則相・不規則相合金のネール温度、伝導特性、熱膨張特性、圧力中における物性に関する研究結果をまとめたものであり、材料物性学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。