氏名	朴　　成　烈
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論文審査委員	主　査　教　授　安藤正海
	教　授　那須奎一郎
	教　授　宮原恒昱
	教　授　中島哲夫
	助教授　雨宮慶幸
	助教授　圓山　裕（岡山大学）

Study on Magnetic Circular Dichroism of Ni, Co, Fe Metals and (Ni, Co, Fe)-Pd Alloys

Serng-Yerl Park

Investigation on metallic magnetism has been a controversial subject of modern science for a long time. The magnetic properties of metals and alloys have usually been considered by two models. One is a localized model where electrons with the magnetization have an atomic character, and also have a state similar to those in an atom inside the crystal. Hence the electrons with respect to the magnetic moment are regarded to be localized in the atomic site, and the total spin is ruled mainly by Hund's rule. Thus the magnetic moment of respective atom is produced, possibly giving rise to ferromagnetism. The model has well described the magnetic properties of rare-earth metals, because 4f electrons with the magnetic moments are well localized inside the atoms, and the orbital is not superposed on the orbitals around an adjacent atom. The other is an itinerant model where the electronic structure for magnetic materials was described by the energy band structure. The itinerant model explains magnetic property as the difference of occupancies by up-spin and down-spin electrons neglecting the orbital moments, thus giving rise to ferromagnetism. Since early theories of magnetism based on these two mutually opposite models had complementary merits and demerits, famous controversies over these two models have lasted for quite a long time. In the early 1970s remarkable process was made by the success of self-consistent renormalization theory of spin fluctuations. The concept of spin fluctuations which also include the Stoner excitation in special cases is now generalized to include both the local and

extended moment limits and a theory of interpolation between them was expected to lead to a unified description of magnetism.

On the other hand, one of the most striking difficulties of the Stoner excitation theory was found by H. C. Siegmann in the spin-polarized photoemission experiment in nickel. If the Stoner splitting ΔE exists in Ni, it necessarily generates a negative polarization at the Fermi energy. ΔE does not appear in the energy distribution curves of photoelectrons from Ni, and quite consistently with this, one does not find any negative polarization of photoelectrons. Therefore more independent and straightforwardly interpretable measurements are required. Because effects of the crystal field largely affects the orbital magnetic moment separation of a spin and orbital parts has become a major experimental target. One of the interesting results has been obtained for this purpose using magnetic circular dichroism (MCD). Here circular dichroism (CD) is the difference between the optical response for the right circularly polarized and the left circularly polarized lights that have the same wave length. Especially CD with magnetic field is known as MCD. Along with the recent development in the circularly polarized synchrotron-radiation, MCD has increasingly become more and more important, both experimentally and theoretically.

In this research we have made MCD experiments in the Ni, Co, Fe 2p, 3p and Pd 3p and 4p excitation regions for Ni, Co, Fe and (Ni, Co, Fe)-Pd alloys. The MCD spectra in the Ni, Co, Fe 3p and Pd 4p excitation regions were measured using an apparatus with permanent magnet flipper at the beamline, BL28A, of the Photon Factory. The MCD spectra in the Ni, Co, Fe 2p and Pd 3p excitation regions were measured with the same apparatus at the beamline, NE1B, of the TRISTAN Accumulation Ring (AR). At both beamlines circularly polarized light was supplied with a helical undulator, with which almost 100%

circularly polarized light would be obtained at the peak of the first harmonic of the undulator radiation. The MCD measurements on the 4d $\rightarrow$ 4f, εf excitation region of rare earth materials were also performed to clarify the origin of the extended MCD and to show the characteristics of the localized moment systems. Furthermore we constructed an advanced chamber equipped with the deposition system with two e-beam evaporation sources, and with a moving photomultiplier detector. Using this chamber we extend our study to thin films of Ni-Pd alloys.

First the starting samples are bulk alloys which were made using an Ar arc furnace and annealed. We obtain the MCD signal which was recorded by measuring the total photoelectron yield, and was normalized with the photon flux determined by the measurement of the total photoelectron yield of Au. The method reported here detects the total yield of electrons as the sample drain currents using a pico-amperemeter. The MCD spectra were measured in such a way that the drain currents were measured for both directions of the applied magnetic field at each photon energy scanned by the monochrometer. The sample surfaces were filed in the vacuum chamber before a series of measurements.

Secondly, thin films of Ni-Pd alloy were prepared on Si(111) substrate by e-beam evaporation. The Si(111) substrate was attached on the sample holder. The evaporation was carried out in the evaporating chamber. The alloy films were obtained by simultaneous evaporation with two evaporation sources. Composition of samples was controlled by adjusting the deposition rate, where both the crystal of the thickness monitor and the substrate were cooled by liquid nitrogen. After evaporation was carried out, MCD measurement with the photoelectron yield was immediately performed in the main chamber.

On the other hand, we have also made MCD experiments in the photoabsorption by the thin films of rare-earth metals. We found that Gd or Eu showed disappeared orbital magnetic moment by 4f electrons, and that Tb, Dy, and Ho have non-vanishing orbital magnetic moment. The extended MCD signals were clearly seen in the photon energy regions lower than the prethreshold and higher than the giant structure for Tb, Dy, and Ho. We additionally found that the Gd or Eu could have small orbital magnetic moment by 5d electrons.

Next we measured the MCD spectra for Ni, Co, Fe metals and (Ni, Co, Fe)-Pd alloys. First we observed the MCD spectra at the Ni, Co, Fe 2p excitation regions and Pd 3p excitation region of the above systems at AR. In the Ni, Co, Fe 2p excitation region ($L_{2,3}$) the MCD signal is negative in the lower energy region and positive in the higher energy region. Also the MCD signal of Pd 3p is similar; it is negative in lower energy region and positive in the higher energy region. This shows that the spin orientation of Pd is the same as that of corresponding metals.

At the $L_{2,3}$ edges the energy integrated value of the MCD in the alloy increase with increasing Pd concentration. Through the linear relation between the integrated MCD signal and the orbital angular momentum $\langle L_z \rangle$, we know that the MCD signal at the $L_{2,3}$ edges shows an enhanced orbital moment compared to that in the pure 3d metals. In pure Ni we also observed the "6 eV" hole-hole correlation satellite in the photoelectron yield spectrum, and these correlation effects appear a distinct shoulder (4 eV satellite) in the MCD spectrum. On the other hand, the number of 3d holes was estimated as the spectral intensity divided by the concentration of corresponding 3d metal. It is easy to estimate the spectral profile after subtracting an arc tangent-like function, which is often adopted in analysis of photoelectron spectra. Also we

assumed that the number of 3d holes is proportional to the total magnetic moments. In Ni_xPd_{1-x} (x=1, 0.5, 0.2) series, the orbital momentum increased with increasing Pd concentration, but for x=0.2 concentration the number of 3d holes seemed to be decreased. We consider that this is caused by the s-like to d-like electron transfer from Ni atomic site to Pd atomic site due to mixing between Ni 4s and Pd 4d states. This strongly induces us to think about a case where the local charge is not conserved in alloying. In Co_xPd_{1-x} (x=1, 0.53, 0.32) series, the number of 3d holes does not increase, although the orbital momentum increase for the increasing Pd concentration. However, in Fe_xPd_{1-x} (x=1, 0.46, 0.23) series both the number of 3d holes and the angular momentum increase with decreasing x. These results show variety of the change transfer depending on the elements and the concentration of the present alloy systems.

We also observed the MCD spectra at the Ni, Co, Fe $M_{2,3}$ edges and at the Pd 4p excitation region of the present systems. The main band of the 3p MCD show the negative sign. In pure Ni 3p excitation region, we do not see the positive contribution in the higher energy region (M_2), which is predicted by localized model. Therefore we see that the spectra in the 3p excitation region should be considered with the itinerant model in one aspect. However we observed the small extended MCD signal which is the characteristics of the localized model. This is not in good agreement with the calculation by G. van der Laan et al., which is based on the impurity Anderson model with configuration interaction between $3p^53d^{10}\underline{L}$ state and $3p^53d^9$ state, considering full atomic multiplets. On the other hand, in Pd 4p excitation region the MCD spectrum of the 3d metals was changed by Pd. Especially the MCD spectrum of $Co_{.32}Pd_{.68}$ alloy has a sharp peak at Co 3p edge. We consider that this is partly caused by the spin-dependent band spectrum resulting from the effect of the

density of state and that it also reflects many-body screening effect due to spin-dependent core hole potential.

It is important to notice that the apparent difference of the estimated number of 3d holes as well as the 3d orbital moments between the $L_{2,3}$ data and $M_{2,3}$ data comes from the fact that we see more of the s-like final states in $M_{2,3}$ measurements. Through the comparison with the $M_{2,3}$ and the $L_{2,3}$ data we can obtain the detailed information on the direction and the amount of the electron transfer and its symmetry (s-like or d-like).

Finally we also obtained similar MCD spectra Ni 3p and Pd 4p excitation regions for Ni-Pd thin films on Si(111) substrate, which indicates that the bulk materials are still good for the present measurements.

In conclusion it has been found in the study:

1) Comparison between 3p MCD and 2p MCD of 3d transition metals clarifies the details of the charge transfer and the magnetic moment due to alloying.

2) In fact the electron transfer from Pd 4d states can make a 4s-like state around Ni, Co, or Ni atomic site and 3d states can make a 5s-like state around Pd due to one-body mixing. The direction and the amount of the transfer are checked both by the estimation of the number of 3d holes and the orbital moment.

3) In the present system the above transfer depends on the 3d elements. There is no systematic tendency which could be predicted by a localized model, though the spin dependent density of states plays the essential role to determine the number of 3d holes.

4) The extended MCD in the low energy data for rare earth metals is strong atomic character of $4d \rightarrow 4f$, εf excitation and the subsequent relaxation process.

5) The above extended MCD were also observed in 3d metal-Pd system, indicating that the atomic continuum states should be considered even in the atomic model to explain the experimental results.

6) There is no satisfactory theory to explain the MCD spectra of the present alloy system. For example, the band calculation based on the conservation of the local charge with d-symmetry does not hold in interpretation of the present MCD spectra.

7) Thus the present results could be explained considering both the atomic and itinerant characters. They would give warning to the band theory which explains the magnetic moment only in terms of the difference between the up-spin and the down-spin occupancy, while they also gives criticism to the atomic model based on the impurity Anderson model.

博士論文審査結果の要旨

朴君の学位論文は、典型的な遍歴磁性体である金属Ｆｅ、Ｃｏ、Ｎｉ及びそれに「強磁性一歩手前」といわれるＰｄを加えて合金化した試料について、円偏光放射光を利用して磁気円二色性を測定し、磁性状態を解析したものである。

物質の磁性の起源を説明するモデルとして、古くからバンド理論を基礎とした遍歴モデルと局在スピン系を出発点とする局在モデルの２つの流れがあり、またスピン系の揺らぎを取り入れた両者を結びつけようとする理論も提案されているが、決着がつかないままになっている。とくに最近ＮｉやＦｅについてのスピン分解能光電子分光の結果はＭｏｒｉｙａ理論(局在と遍歴を「統一」したといわれる)との矛盾を明らかにしてばかりではなく、非常に大きな局在的な電子相関効果を反映していると思われる結果が得られて、そもそも遍歴電子系の強磁性の発現機構は何かという困難につきあたっている。

本研究では、Ｆｅ、Ｃｏ、ＮｉにＰｄを加えたとき、それぞれの原子サイトの全磁気モーメント・軌道磁気モーメントの変化を、異なる内殻励起による磁気円二色性のデータを比較しながら、磁気モーメントの総和則を批判的に適用して、解析するというユニークな方法論を採用している。そもそも、内殻励起磁気円二色性のデータは、中性子回折と比べて、磁気モーメントのスピン部分と軌道部分を分離できるという優位性が世界的に主張されてきたが、このことは磁気モーメントの総和則の注意深い適用によってのみ可能である。朴君は、Ｆｅ、Ｃｏ、Ｎｉの３ｐ内殻励起の磁気円二色性データと２ｐ内殻励起磁気円二色性のそれが、形式的に総和則を適用すると、異なった磁気モーメントの値を与えることを見だし、逆にこの見かけの差から、磁気モーメントを担う電子の局在性の度合や、合金化に伴う電荷移動の性格を明らかにした。具体的にはＮｉとＣｏについてはＰｄを加えると、原子１個当たりの軌道磁気モーメントが著しく増大し、スピン部分はあまり変わらないこと、Ｆｅ－Ｐｄ系では結晶構造の変化を反映して複雑な振る舞いが見られること、また合金化による電荷移動は、ＮｉとＦｅについては、これら４ｓ的電子がＰｄの４ｄホールを埋めてＰｄの磁気モーメントを下げていること、さらに２ｐ内殻励起の場合、ＮｉとＣｏには局在的な３ｄ－３ｄ電子相関が明瞭に見出されるＰｄで希釈するとその影響は小さくなること、等様々な知見が得られた。さらに重要なことは、Ｅｂｅｒｔらによる最も進んだ相対論的バンド計算から見積もられた軌道モーメントとスピンモーメントの比と、この研究による結果が大きく異なっていること、他方、不純物アンダーソンモデルのような局在モデルとも一致せず、この研究の磁気円二色性のデータを説明するには、現存する局在理論、遍歴理論のどちらでも不十分であると結論づけている。

朴君の研究は、上記の合金試料についての内殻励起磁気円二色性のデータを世界初めて測定したのみならず、二種の異なる内殻励起を利用して数多くの知見を得て、遍歴電子系の磁性記述が単純でないことを明らかにしており、学位論文として十分な内容を持つと認められる。