Magnetovolume Effects in Strongly and Intermediately Correlated Electron Systems

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Analyses of magnetovolume effects such as the forced volume magnetostriction and the thermal expansion anomaly can give estimation of local amplitude of spin fluctuations. We have shown that bcc Fe has a rigid magnetic moment and that the magnetic moment of Invar type alloys is rather soft. It is pointed out that the total energy difference between the magnetized state and the nonmagnetic state obtained by self-consistent energy band calculations using a local-spin-density approximation is much higher than the Curie temperature for rigid spin systems and comparable for soft spin systems. The effects of zero point spin fluctuations observed in the YMn₂ system are discussed.

§ 1. Introduction

Recent developments in the theory of spin fluctuations give a framework for solving the controversial debate between the local moment model and the Stoner-Wohlfarth model for magnetism of transition metals. In particular, the self-consistent renormalized theory successfully explained many respects of weakly or nearly ferromagnetic metals. On the other hand, the understanding of magnetism in strongly or intermediately correlated electron systems is not satisfactory. The ground state properties such as the value of spontaneous magnetization of ferromagnetic transition metals are well explained on the basis of band calculations by taking into account the correlation effects as the local spin density potential. For ferromagnetic substitutional alloys, the coherent potential approximation has been successfully applied to estimate the atomic moment of each element. However, the quantitative understanding of excited states is far from the final stage. Among them the temperature dependence of amplitude of local spin fluctuations, \( S_L \), below and above the Curie temperature is a crucial quantity for characterizing the magnetism and thermodynamic properties of magnetic metals. Experimentally, the amplitude of spin fluctuations can be, in principle, estimated by neutron scattering. However, scanning in a wide range of the momentum and energy space is necessary for reliable estimation of \( S_L \), which is hardly attained in the present neutron facilities.

We have pointed out that the increase in the 3d band polarization should give rise to a volume expansion through the mechanism given below. The band polarization causes an increase in the kinetic energy. The cost of the kinetic energy can be saved by a volume expansion because the 3d band width \( W \) is highly dependent on the atomic separation \( R \), like \( W \propto R^{-5} \). The increase in the kinetic energy is propor-
tional to the square of magnetization, $M$, in the first approximation. Therefore, the volume change due to the band polarization may be given by $\Delta V/V = \omega_m = kM^2$. Self-consistent spin polarized energy band calculations have shown that this volume expansion is sizable to be several percent for bcc Fe. However, such a large volume change is not observed in Fe at the Curie temperature, implying that the Stoner-Wohlfarth theory does not work in strongly correlated electron systems such as bcc Fe. The apparent lack of this giant volume change expected from the band calculation can be explained as that the effective $3d$ band splitting does not change at $T_c$ and persists as a local moment above $T_c$. In terms of the spin fluctuation theory, the amplitude of longitudinal spin fluctuations remains almost constant below and above $T_c$.

On the other hand, we have pointed out through analyses of the lattice parameter of $3d$ metal alloys that the atomic volume of $3d$ atoms expands when they are locally magnetized. The magnitude of the expansion is given by $\omega_m \sim km^2$, where $m$ is the magnitude of local moment. The proportionality constant $k$ is roughly $10^{-2}/\mu_b^2$, which is comparable to the result of the band calculation. When the magnitude of a local moment, $m=2S_L$, varies with temperature, a notable thermal expansion anomaly should be observed. Therefore, analyzing thermal expansion curves properly, we can estimate the temperature dependence of $S_L^2$. We have developed a phenomenological theory of magnetovolume effects taking into account both effects of longitudinal and transverse spin fluctuations and analyzed thermal expansion curves of typical transition metals and alloys. In this paper, we discuss the temperature dependence of the amplitude of local spin fluctuations in some selected materials which show typical thermal expansion curves, referring to recent experimental results and band calculations.

§ 2. Phenomenological description of magnetovolume effects

We have proposed that the correlation between the volume change and the local magnetic moment may be given by the sum of two contributions, namely, the volume change caused by a change in the magnitude of local moments, or the change in the effective band polarization, and that caused by a change in relative orientations of neighboring local moments, as given by the following equation,

$$\omega_m = k \cdot \sum m_i^2 + k' \cdot \sum \langle m_i \cdot m_j \rangle,$$

where $k$ and $k'$ are coupling constants between the volume and longitudinal and transverse spin fluctuations, respectively. $\langle m_i \cdot m_j \rangle$ represents the correlation function of local moments, which may be approximated by $\langle m_i \cdot m_j \rangle \sim \mu_s^2$ ($\mu_s$ the spontaneous magnetization per atom) for a ferromagnet well below the Curie temperature. We have shown that $k$ is fairly large as about $10^{-2}/\mu_b^2$ for $3d$ transition metals and $k'$ is much smaller than $k$.

$\omega_m$ itself is not a directly measurable quantity. In this paper, we mainly refer to the spontaneous volume magnetostriction, $\omega_s$, which is a volume change accompanied with magnetic ordering and the forced volume magnetostriction, $d\omega/dH$. The former
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\[ \omega_s(T) = \omega_m(T) - \omega_m(T \gg T_c) = k(m(T)^2 - m(T \gg T_c)^2) + k' \mu_s^2, \]

where \( m(T) \) means the magnitude of a local moment at a temperature \( T \). Since \( k \gg k' \) we can expect a large spontaneous volume magnetostriction only when \( m(T) \) itself decreases with increasing temperature below \( T_c \). The forced volume magnetostriction is given by,

\[ \frac{d\omega}{dH} = 2M(T)[k \chi_d(T) + k' \chi_{sw}(T)], \]

where \( M(T) \) is the magnetization, \( \chi_d \) the Stoner susceptibility due to 3d band polarization and \( \chi_{sw} \) the spin wave contribution to the high field susceptibility. Since \( \chi_{sw}(T=0)=0 \) and therefore \( \chi_{ht}(0) \approx \chi_d \), we can estimate \( k \) experimentally. If the spin wave dispersion coefficient \( D \) is available, we can estimate \( \chi_{sw}(T) \) and consequently \( k' \). Once we have got \( k \) and \( k' \), it is possible to obtain \( m(T) \) from Eq. (1), provided that the thermal expansion due to lattice anharmonicity is properly estimated. In the following section, we review the temperature dependence of longitudinal spin fluctuations, \( m(T) \), of some typical magnetic substances on the basis of the present analysis and discuss the results by comparing the recent band calculations which provide the total energy as a function of the lattice constant for magnetized and nonmagnetic states.

§ 3. Temperature dependence of \( m(T) \)

in strongly and intermediately correlated systems

3.1. \textit{bcc iron}

It is possible to estimate \( k \) from experimental values of \( \frac{d\omega}{dH} \) and \( \chi_{ht} \) at 4.2 K. However, there is an ambiguity due to some other contributions to \( \chi_{ht} \) than \( \chi_d \) such as the orbital susceptibility. Since there is a reliable band calculation for \( \chi_d \), we employed a theoretical value of \( \chi_d \) for estimation of \( k \) of bcc Fe and obtained \( k=0.5 \times 10^{-2}/\mu_b^2 \). The increase in \( \chi_{ht} \) with increasing temperature is fully explained from the increase in \( \chi_{sw} \). On the other hand, \( \frac{d\omega}{dH} \) does not change with temperature within the experimental accuracy. This means that \( k' \) is negligibly small from Eq. (3). Therefore, a giant spontaneous volume magnetostriction would be expected if \( m(T) \) disappeared above \( T_c \) as the Stoner-Wohlfarth theory predicts. The temperature dependence of the thermal expansion coefficient of bcc Fe near the Curie temperature is shown in Fig. 1. A small dip is observed at \( T_c \). However, the spontaneous volume magnetostriction, which can be evaluated by integrating the thermal expansion

![Graph](https://example.com/graph.png)

Fig. 1. Temperature dependence of the thermal expansion coefficient of Fe.
coefficient curve, is as small as $\omega_s(T=0)=14 \times 10^{-4}$. From Eq. (2), we can say that the decrease in the magnitude of local moment of Fe up to $T_c$ is at most 0.1 $\mu_B$. Thus, we may conclude that bcc Fe is a strongly correlated system and the 3$d$ band polarization remains almost unchanged above $T_c$ as a local magnetic moment.

Moruzzi et al. have calculated the total energy contour map of bcc Fe in the magnetic moment and atomic-size space by a self-consistent band calculation using a local-spin-density (LSD) approximation. The equilibrium point is at $m=2.15$ $\mu_B$ and $r_{WS}=2.63$ a.u., which is in good agreement with the experiment. The atomic radius for a nonmagnetic state is 2.56 a.u. Therefore, the volume of the magnetic state is larger than that of the non-magnetic state by 8%. The calculated value gives $k=1.7 \times 10^{-2}/\mu_B^2$, which is a little larger than the experimental value. The energy difference between magnetic and nonmagnetic states is 23 mRy, that is, 3600 K, which is 4 times as large as $k_B T_c$. This means that the local moment is fairly stable in the temperature range up to $T_c$ in consistent with the conclusion of the analysis of magnetovolume effects.

3.2. Invar alloy: Fe-35%Ni

It is well known that Fe rich fcc iron alloys such as Fe-Ni and Fe-Pt, which are called the Invar type alloy, exhibit remarkable magnetovolume effects. Among them, the Fe-35Ni Invar alloy is most extensively studied in many respects. The most distinct characteristic of the Invar alloy is a large spontaneous volume magnetostriction, which leads to a low thermal expansivity as shown in Fig. 2. Noting the concentration dependence of lattice parameter of fcc Fe-Ni alloys below and above the Curie temperature, we have shown that collapse or shrinkage of local moments above $T_c$ is the origin of the large spontaneous volume magnetostriction.

We have estimated the temperature dependence of the magnitude of local moment in the Fe-35Ni Invar alloy on the basis of the present phenomenological theory. From the values of $d\omega/dH$ and $\chi_{HT}$, $k$ is estimated as $0.9 \times 10^{-2}/\mu_B^2$. Using the value of spin wave stiffness constant $D=110$ meV, it is possible to separate the high field susceptibility into $\chi_d(T)$ and $\chi_{SW}(T)$. As a result of this analysis, it has been revealed that the increase in $d\omega/dH$ with increasing temperature can be mostly ascribed to the increase in $\chi_d(T)$, implying $k'$ is again negligibly small in this system. Assuming $k'=0$ and neglecting the contribution of Ni to $\omega_s$, we can estimate the shrinkage of local magnetic moment of Fe atom $m_{Fe}(T)$ from Eq. (2) using $\omega_s=1.9 \times 10^{-2}$. We obtained $m_{Fe}(T>T_c)=1.4 \mu_B$, which is much smaller than $m_{Fe}(0)=2.6 \mu_B$. This value is in good agreement with that obtained by neutron scattering.

The total electron energy of the
Fe₃Ni ordered alloy, whose electronic structure would be close to that of Fe-35 Ni disordered alloy, has been obtained by a self-consistent band calculation using an LSD approximation. The result is shown in Fig. 3 as a function of the Wigner-Seitz radius. It should be noted that the total energy difference between the magnetic ground state with $\mu_{Fe} \approx 2\mu_0$ and the nonmagnetic state with a smaller volume is as small as 1.2 mRy, which corresponds to 200 K. This means that the magnetic moment in this system is quite unstable and is easily collapsed by raising temperature, giving rise to a relative volume shrinkage. In terms of spin fluctuations, the stiffness of longitudinal spin fluctuations is low and the amplitude remarkably changes with temperature. We believe that this is the essentials of Invar effects.

3.3. Laves phase compounds

Laves phase intermetallic compound AT₂ is one of the most popular intermetallic compounds containing transition metals, T. They exhibit wide varieties of magnetism depending upon the combinations of A and T elements. Some of them show the Invar type thermal expansion, indicating the instability of local moments.

3.3.1. AFe₂

Figure 4 shows the thermal expansion curves of AFe₂. Since there are not enough data to estimate the coupling constants $k$ and $k'$, it is not possible to perform a quantitative analysis of $m(T)$ for these compounds. In Table I, the magnitude of $\omega_s$ and the energy difference between magnetic and nonmagnetic states calculated using an LSD approximation, are given with other fundamental magnetic properties. It should be noted that the energy difference is largest for YFe₂, which does not show a thermal expansion anomaly at $T_c$, implying high stability of Fe moment. On the other hand, the energy difference of ZrFe₂ and HfFe₂, which have a fairly large spontaneous volume magnetostriction, is much smaller than...
Table I. Fe magnetic moment $\mu_{\text{Fe}}$, Curie temperature $T_c$, spontaneous volume magnetostriction $\omega_s$ and the energy difference between the ferromagnetic state and the non-magnetic state of ferromagnetic Fe Laves phase compounds.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_{\text{Fe}}(\mu_B)$</th>
<th>$T_c$(K)</th>
<th>$\omega_s \times 10^{-3}$</th>
<th>$\Delta E$(mRy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrFe$_2$</td>
<td>1.6</td>
<td>630</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>HfFe$_2$</td>
<td>1.36</td>
<td>591</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>ScFe$_2$</td>
<td>1.37</td>
<td>542</td>
<td>5.5</td>
<td>17.5</td>
</tr>
<tr>
<td>YFe$_2$</td>
<td>1.4</td>
<td>554</td>
<td>$\sim$0</td>
<td>25</td>
</tr>
</tbody>
</table>

that of YFe$_2$, indicating a less stable Fe moment in these systems.

3.3.2. $ACo_2$

It has been believed that YCo$_2$ is just on the verge of possessing a magnetic moment on a Co atom. Its magnetic susceptibility is strongly enhanced. Recently, an itinerant electron metamagnetic transition has been found at low temperatures for YCo$_2$ and the Y(Co$_{1-x}$Al$_x$)$_2$ systems. A large volume expansion, which can be ascribed to the onset of Co moment of about 0.5 $\mu_B$, was observed at the metamagnetic transition point. The Co moment is also metamagnetically induced by the exchange fields from rare earth spins in RCo$_2$ compounds. Therefore, the induced magnetic moment on Co sites should disappear above the Curie temperature. We have shown that all RCo$_2$ compounds exhibit a distinct thermal expansion anomaly at $T_c$. The volume expansion below $T_c$ is comparable to the volume change observed in metamagnetic transition of YCo$_2$, indicating that the Co moment collapses above $T_c$.

3.3.3. YMn$_2$ and related compounds

Recently, it was found that YMn$_2$ is an antiferromagnet with Mn moment of 2.7 $\mu_B$ and $T_N \sim$ 100 K, the magnetic structure of which is shown in Fig. 5. A precise neutron diffraction study has shown the antiferromagnetic structure is helically modulated with a period of about 400 Å. The magnetic transition is of the first order. Above $T_N$, the susceptibility increases with increasing temperature, indicating the absence of well-defined local moments in the paramagnetic phase. Striking features of this material are a huge volume expansion of about 5% in the antiferromagnetic state and an enhancement of the thermal expansion coefficient above $T_N$ as shown in Fig. 6. For an antiferromagnet, it is not possible to estimate the magnetovolume coupling constants $k$ and $k'$ from the magnetostriction. Noting the fact that these thermal expansion

Fig. 5. Spin structure of YMn$_2$. Only Mn sites are shown. Open and closed circles represent Mn atoms with up down spins. Recent neutron diffraction study has revealed that this antiferromagnetic spin arrangement is helically modulated with a period of about 400 Å.
anomalies disappear by substituting Al for Mn, we have estimated the temperature dependence of the local amplitude of spin fluctuations on Mn atoms by analyzing the
lattice parameter and the thermal expansion curves of the Y(Mn$_{1-x}$Al$_x$)$_2$ system. From this analysis, we have given a conclusion that the Mn moment does not completely collapse above $T_N$ and it increases with increasing temperature as shown in Fig. 7.

Neutron scattering measurements have been carried out for this compound to estimate magnetic moments in the paramagnetic state.$^{25,26}$ The result is also shown in Fig. 7. It was found that the magnitude of magnetic moment drops to 1 $\mu_B$ at just above $T_N$ from 2.7 $\mu_B$ in the antiferromagnetic state and then increases with increasing temperature in agreement with the above analysis. The increase in the magnetic moment may be explained by thermal excitations of longitudinal spin fluctuations with increasing temperature. The enhancement of the thermal expansion coefficient above $T_N$ has been explained as a result of thermally induced spin fluctuations.$^{24}$ It should be noted, however, that the value of Mn moment determined by neutron scattering is a little larger than that estimated by the analysis of thermal expansion curves. The origin of this disagreement is discussed later.

A band calculation has been carried out for this material by the LMTO method within the framework of LSD approximation.$^{17}$ The total energy calculated for the antiferromagnetic state and the paramagnetic state as a function of the lattice parameter is given in Fig. 8. It should be noted that the energy difference between the antiferromagnetic and paramagnetic states is considerably small as 3 mRy and the equilibrium volume of the paramagnetic state is smaller than that of the antiferromagnetic state by 4.5%. This result explains why the antiferromagnetic state is easily collapsed into the nonmagnetic state with a smaller volume by thermal energy.

It is an interesting problem to know whether the amplitude of spin fluctuations in the paramagnetic state vanishes or remains finite at 0 K. We found that the paramagnetic state is easily stabilized down to 0 K by applying pressure$^{27}$ or substituting Sc for Y.$^{28}$ Figure 9 shows the temperature dependence of the lattice parameter of Y$_{1-x}$Sc$_x$Mn$_2$. The volume expansion due to antiferromagnetic ordering disappears by only 2% substitution of Sc for Y. NMR measurements have confirmed that there is no indication of magnetic ordering even at 0.07 K.$^{29}$ We have carried out paramagnetic neutron scattering measurements for Y$_{0.97}$Sc$_{0.03}$Mn$_2$. The result is shown in Fig. 10. Unexpected large scattering has been observed at the lowest temperature, indicating the existence of large zero point spin fluctuations. A crude estimation of the amplitude of the zero point spin fluctuations gives 1$\mu_B$ per Mn atom. This observation indicates that the ground state of this material cannot be simply
described as the nonmagnetic state in the sense of the Hartree-Fock approximation. Therefore, it is not clear that the paramagnetic moment determined by neutron scattering can be straightforwardly compared with that responsible for magnetovolume effects. Analyses of thermal expansion curves of YMn$_2$ and related compounds indicate that only thermally excited spin fluctuations couple with the volume.\textsuperscript{30} However, no theoretical justification for this fundamental problem has been given so far.

§ 4. Concluding remarks

Analyses of magnetovolume effects such as the forced volume magnetostriction and the thermal expansion anomaly can give estimation of the local amplitude of spin fluctuations. We have shown that bcc Fe has a rigid magnetic moment over the whole temperature range. The magnetic moment of Invar type alloys, including Laves phase compounds, which show distinct thermal expansion anomalies, is fairly soft. It was pointed out that the total energy difference between the magnetized state and nonmagnetic state calculated in the framework of LSD approximation, is much
Fig. 10. Wave vector dependence of the paramagnetic neutron scattering $S(Q)$ of $Y_{0.91}Sc_{0.09}Mn_2$ at 8 K, 120 K and 330 K. Arrows indicate the positions of magnetic Bragg peaks.

higher than the Curie temperature for rigid spin systems and comparable for soft spin systems. It is likely that the giant zero point spin fluctuations observed in the $Y_{0.97}Sc_{0.03}Mn_2$ system do not couple with the volume. We hope that the effects of zero-point spin fluctuations on the total electron energy is discussed by theorists.

Acknowledgements

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