Density functional calculations are performed to investigate the phase transition in FeRh alloy. The effective exchange coupling, the critical temperature of magnetic phase transition and the adiabatic spin wave spectrum have been obtained. Different contributions to the free energy of different phases are estimated. It has been found that the antiferro-ferromagnetic transition in FeRh occurs mostly due to the spin wave excitations.

The antiferromagnetic (AFM) - ferromagnetic (FM) phase transition in FeRh with the ordered CsCl structure has been intensively studied both experimentally and theoretically. This transition occurs at $T_{tr} \approx 340$ K without any accompanying structural changes, although there is an abrupt 1% volume expansion. At low temperatures the magnetic configuration of FeRh is the type-II AFM (successive layers of (111) Fe planes AFM coupled) with moments $3.3 \mu_B$ on Fe atoms (Rh atoms are nonmagnetic). Above $T_{tr}$ in FM phase magnetic moments are $3.2 \mu_B$ on Fe atoms, $1.0 \mu_B$ on Rh atoms and the Curie temperature ($T_C$) is $\approx 670$ K. In addition, it was found that $T_{tr}$ is increased with pressure. The AFM-FM transition can also be induced by applying external magnetic field, whose critical value at zero temperature is about 300 kOe and smaller at higher temperatures, making this material a natural magnetic sensor.

Early theories of this transition based on the exchange-inversion model, which assumes a change of sign for the exchange parameter at some volume, can not account for the experimental observation of the large entropy changes at $T_{tr}$. After discovering that the electronic specific heat in the FM phase is nearly four times larger than in the AFM phase, Tu et al. proposed that the change of the band electron entropy plays a major role in this transition. However, the magnitude of their free energy change appears too small to compensate the internal energy loss for the transition to occur. So far, in spite of many years of research, there has been no convincing explanation of the nature of the phase transition in FeRh.

In this paper we study this transition using first principles calculations and the non-collinear version of the linear muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA). In the local spin density approximation (LSDA) we use the von Barth-Hedin potential, and for the nonlocal corrections the Langreth-Mehl-Hu functional, the relativistic effects and the combined corrections are included. For the radii of atoms, the ratio $R_{Rh}/R_{Fe} = 1.03$ was used. The self-consistent calculations are performed for the different lattice parameters for FM and AFM states using a spin spiral approach. The gradient corrections are expected to be important in Fe-rich BCC based systems due to well known fact that LSDA predicts, for instance, the wrong FCC ground state pure Fe. Below we will show that it is exactly a case in FeRh. Using electronic density of states (DOS) and exchange parameters, we calculate the free energy change of the AFM and FM states. Various thermal quantities related to the AFM-FM transition, including the transition temperature, its pressure dependence, the entropy and the specific heat changes are calculated and compared with the corresponding experiments. According to our calculations, the AFM-FM
transition in FeRh appears primarily due to the magnon (spin wave) excitations.

Fig. 1 (a) shows the calculated energy of the AFM and FM states. In LSDA the equilibrium Wigner-Seitz radius $R_{WS}$ for the AFM (FM) phase is 2.767 (2.780) a.u., which is smaller than the previous non-relativistic result 2.782 (2.798) a.u.\(^\text{[12]}\) (our non-relativistic result is 2.789 (2.803) a.u.). The energy difference between the AFM and FM states at their respective equilibrium $R_{WS}$ is 1.89 mRy/atom. With nonlocal corrections this energy difference is reduced to 0.206 mRy/atom, which is in agreement with the experimental value 0.196 mRy/atom\(^\text{[3]}\). Other results are listed in Table I.

Only collinear AFM and FM configurations were observed in the experiments. In our calculation, however, we found that without nonlocal corrections the FM configuration is not a locally stable state with respect to the magnetic moment deviations, as is shown in Fig. 1 (b) (two kinds of noncollinear configurations are considered). In both those states the Fe atoms are divided into two sublattices, identical to that in the type-I (successive (001) Fe layers belong to the different sublattices) and type-II AFM states with the angle $\theta$ between Fe magnetic moments from the different sublattices, while the moments of Rh atoms are parallel to the sum of the Fe moments. Such instability of the FM state is removed if the nonlocal corrections are taken into account. Results from Fig. 1 (a) and (b) suggest that the nonlocal corrections are important in FeRh and necessarily should be taken into account in the investigation of the phase transition.

Using formalism from Ref.\(^\text{[21]}\) we calculated the parameters of the exchange coupling. The obtained parameters are different for the FM and AFM configurations (see Table II). To estimate the magnetic contributions to the free energy we calculated the magnon spectrum in both phases. In the adiabatic approximation for the AFM state $\omega_{AFM}^q = (2g_\mu B/m_p e)\sqrt{J_0 - J_q/(J_0 - J_q + Q)}$, with $J_q = \sum_{i,j} J_{ij} e^{iq \cdot \mathbf{R}_{ij}}$ being the Fourier transformation of $J_{ij}$ in AFM state and $Q = (\pi \pi \pi)$. For the FM state $\omega_{AFM}^{\pm q} = g_\mu B(A_q + B_q \pm \sqrt{(A_q - B_q)^2 + 4X^2_q})$, where $A_q = (J_{FeFe}^q - J_{FeRh}^q + J_{FeRh}^q)/m_{Fe}$, $B_q = (J_{RhRh}^q - J_{RhFe}^q + J_{RhFe}^q)/m_{Rh}$, and $X_q = J_{FeRh}^q/m_{Fe} m_{Rh}$, with $J_{FeFe}^q$, $J_{FeRh}^q$, and $J_{RhRh}^q$ being the Fourier transformations of the exchange interactions inside (or between) the corresponding sublattice(s). The magnon DOS obtained from this spectrum is shown in Fig. 2 together with the electronic DOS.

To study the relative stability of the AFM and FM configurations at finite temperatures, let us compare their free energies. Here we consider the contributions from electrons and magnons only. The lattice contribution is neglected because the magnitudes of the bulk moduli and Debye temperatures in both phases are very similar (Table I). The free energy due to band electrons and magnons are given by

$$F_{el}(T) = \frac{1}{2}\{\varepsilon_{F} n - k_{B} T \int d\varepsilon N(\varepsilon) \log(1 + e^{(\varepsilon - \varepsilon_{F})/k_{B} T})\},$$
$$F_{mag}(T) = -\frac{k_{B} T}{2} \int \frac{d\omega}{(2\pi)^3} \log(1 - e^{-\omega/k_{B} T}),$$

where $n$ and $N(\varepsilon)$ are the number of electrons and the electronic DOS, correspondingly. Fig. 3 (a) shows the free energy difference $\Delta F = \Delta F_{FM}^{AFM}$ as a function of temperature. The transition temperature $T_{tr}$, determined from $\Delta F = 0$, is 371 K, which is close to the experimental result $T_{tr} \approx 340$ K. Both contributions are shown, with the main one (more than 80%) coming from magnons. So, the origin of the AFM-FM transition should be attributed primarily to the magnon excitations rather than to pure electronic spectrum modifications. The obtained $\Delta F(T)$ also enables us to get the pressure dependence of the transition temperature, whose experimental value is about $\Delta F/dT \approx 5.1 - 5.8$ K/bar\(^\text{[3, 4]}\). With applied pressure the AFM state gains more free energy $\Delta G = P\Delta V$ (\(\Delta V\) is the volume difference) than the FM state and the derivative $d\Delta G/dP$ is close to $-6.2 \times 10^{-3}$mRy/bar per atom. From Fig. 3 (a) $d\Delta F/dT = -1.17 \times 10^{-3}$mRy/K and from the equilibrium condition $d\Delta F = d\Delta G$ we obtain $(d\Delta F/dP \approx 5.3$ K/bar, which agrees well with the experiments.

From the obtained electronic DOS and magnon spectrum, one can also evaluate various thermal quantities. In Fig.3 (b) we show the calculated differences of the entropy and the specific heat between AFM and FM states as a function of temperature. These two quantities are independent of the zero temperature energy, with their measured values at $T_{tr}$ being $\Delta S^{exp} \approx 13 - 19.6$ Jkg$^{-1}$K$^{-1}\text{[6, 7, 8]}$ and $\Delta C^{exp} \approx 13.6$ Jkg$^{-1}$K$^{-1}\text{[8]}$. Just as the free energy, the calculated contributions to both $\Delta S$ and $\Delta C$ near $T_{tr}$ mainly determined by the magnon excitations. At the calculated $T_{tr} = 371$ K, we obtain $\Delta S = 19.3$ Jkg$^{-1}$K$^{-1}$ and $\Delta C = 15.1$ Jkg$^{-1}$K$^{-1}$, while at $T_{tr} \approx 340$ K, the corresponding values are 17.9 and 15.6 Jkg$^{-1}$K$^{-1}$.

Since the Rh atoms have a nonzero value ($1\mu_{B}$) of magnetic moments in the FM state, this state has more magnetic degrees of freedom. It was proposed that this additional number of degrees of freedom increases the entropy and thus stabilizes the FM state\(^\text{[14]}\). The evaluation of this entropy gain gives $\Delta S \approx N k_{B} \log 2 \approx 36$ Jkg$^{-1}$K$^{-1}$, which is too large compared to the experimental results. According to our calculated DOS of magnon, this picture of extra entropy is not quite accurate. From Fig. 2 (b) one can see that in the FM state the magnon excitations $\omega_{q}^{-}$ and $\omega_{q}^{+}$ are separated by the large energy gap. We call the $\omega_{q}^{-}$ ($\omega_{q}^{+}$) mode to be Fe (Rh)-like, because a similar mode (the dotted line in Fig. 2(b)) can be obtained if we fix the orientations of the Rh (Fe) moments by letting $X_q = 0$ in the expression for $\omega_{q}^{FM}$. Near $T_{tr}$ only the Fe-like mode contributes to the thermal properties so that the number of the effective magnon states in the FM and AFM phases is the same, i.e., there is essentially the same
number of spin degrees of freedom in the FM and AFM states. That does not mean, however, that the nonzero Rh moments in the FM phase do not contribute to the thermal properties. On Fig. 2(b) it is shown that without the movement of the Rh moments there is the energy gap between the ground state and the lowest-energy Fe-like magnons, which significantly influence the thermal properties. A calculation shows that at $T_{TR}$ the magnon free energy (with the orientations of the Rh moments being fixed) is only about one third of that when the Rh moments are not fixed. In other words, the Rh moments soften considerably the stiffness of the Fe-like magnons, significantly influencing the thermal properties. A comparison of the magnon DOS in the AFM and FM states indicates that near $T_{TR}$ it is much easier to excite the Fe-like magnons in the FM state. This is the main reason for the difference in thermal properties between the two phases, and it is also the driving force of the AFM-FM transition in FeRh.

Finally let us evaluate the Curie temperature by using the obtained pair exchange interactions $J_{ij}$. In the mean field (MF) approximation

$$T_{C}^{MF} = \frac{1}{3k_B} \left( J_{0}^{FeFe} + J_{0}^{RhRh} + \sqrt{(J_{0}^{FeFe} - J_{0}^{RhRh})^2 + 4(J_{0}^{RhFe})^2} \right)$$

(2)

From $J_{0}^{FeFe} = -3.56 \text{ mRy}$, $J_{0}^{FeRh} = 9.92 \text{ mRy}$ and $J_{0}^{RhRh} = 0.85 \text{ mRy}$ we obtain $927 \text{ K}$, which is nearly $40\%$ higher than the experimental $T_C \sim 670 \text{ K}$. Our Monte-Carlo calculations (with all calculated long ranged $J_{ij}$ included) produced correspondingly $660 - 690 \text{ K}$, so that the ratio $T_C/T_{C}^{MF} \approx 0.71 - 0.74$ is nearly the same as that of the simple cubic lattice Heisenberg model where $T_C/T_{C}^{MF} = 0.722$ [23]. The agreement of the calculated and the experimental $T_C$ indicates that the Heisenberg model may still work well in the temperature region near $T_C$ in FeRh.

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Fig. 1. The total energy obtained in the local (L) and nonlocal (NL) approximations, represented by open and solid symbols. The total energy for: (a) AFM (circles) and FM (squares) states as a function of $R_{WS}$; (b) for the type-I (squares) and type-II (circles) noncollinear states as a function of the spin spiral angle $\theta$. $R_{WS}$ is fixed at the equilibrium value of the FM state.

Fig. 2. Calculated DOS of FM (solid line) and AFM (dashed line) states: (a) the electronic DOS and (b) the magnon DOS. In (b) the dotted lines correspond to the FM magnon DOS when $X_q = 0$ in the expression for $\omega_{qFM}$.

Fig. 3. The calculated differences of (a) the free energy $\Delta F$, (b) the entropy $\Delta S$ and the specific heat $\Delta C$ between FM and AFM phases. The dashed and dotted lines (short-dashed and short-dotted lines for $\Delta C$) correspond to the contributions from the electrons and magnons, correspondingly. The solid line is their sum.

TABLE I: Calculated physical properties of the AFM and FM configurations of FeRh obtained in the local (first row) and nonlocal approximations. $m_{Fe}$ and $m_{Rh}$ are magnetic moments of Fe and Rh atoms, $B$ is the bulk modulus, $\Theta_D$ is the Debye temperature and $N(\epsilon_F)$ is DOS per formula unit at the Fermi level.

| $R_{WS}$ (a.u.) | $\Delta E$ (mRy/atom) | $m_{Fe}$ ($\mu_B$) | $m_{Rh}$ ($\mu_B$) | $B$ (kbar) | $\Theta_D$ (K) | $N(\epsilon_F)$ (States/Ry) |
|-----------------|----------------------|------------------|------------------|----------|-------------|------------------|
| 2.767(2.780)    | 1.89                 | 3.12(3.22)       | 0(1.04)          | 2454(2364)| 385(379)    | 18.0(29.5)       |
| 2.796(2.807)    | 0.206                | 3.28(3.31)       | 0(1.02)          | 2194(2181)| 366(365)    | 15.6(28.0)       |

TABLE II: Pair exchange parameters (in mRy) in AFM and FM phases of FeRh. Corresponding coordinates are shown in units of the lattice constant.

| Type of pair | $\Delta x$ | $\Delta y$ | $\Delta z$ | $J_{ij}^{AFM}$ | $J_{ij}^{FM}$ |
|--------------|------------|------------|------------|----------------|---------------|
| Fe-Rh        | 0.5        | 0.5        | 1.062      | 0              | 0             |
| Fe-Fe        | 1.0        | 0.0        | 0.104      | 0.008          |               |
| Rh-Rh        | 0.0        | 0.0        | -0.098     | 0.442          | 0.058         |
|              | 2.0        | 0.0        | 0.018      | 0.018          |               |
|              | 1.0        | 1.0        | 0.045      | 0.045          | 0.603         |
(a) $E$ (mRy/atom) vs. $R_{\text{WS}}$ (a.u.)

(b) $E(\theta)$ (mRy/atom) vs. $\theta/\pi$
