Crystalline electric field schemes of Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$

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Abstract. The splitting levels and corresponding wave functions of rare earth compounds Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$ have been presented by taking into account the crystalline electric field. The influences of Ge content on rare earth ion ground state splitting also have been analysed. The first excited energy and overall splitting energy of Ce$_2$NiGe$_3$ coincides with the ones calculated by simulating Schottky specific heat.

1. Introduction

The investigation of crystalline electric field (CEF) effect for 3d-4f rare-earth inter-metallic compounds has become an important subject in the field of magnetism and magnetic materials from both theoretical and application point of view in recent years [1-6]. Although the 4f electron is firmly bound in the depth of atoms, many rare earth compounds appear various electronic interactions related to 4f electron, including magnetic order, Kondo effect, RKKY interaction, heavy electron effect and CEF effect. The multiple ground state of local 4f electron in rare earth compounds under the CEF actions of surrounding ions will be split or excited. The degeneracy may partially or completely disappear, and then producing a great impact on magnetic susceptibility, specific heat, resistivity and magnetization. Therefore, we can stimulate the temperature dependence of the inverse magnetic susceptibility, specific heat, magnetization to obtain the CEF schemes on the bases of CEF theories. For example, the CEF splitting levels of PrNi$_2$Al$_5$ [3], Ce$_2$Pd$_3$Si$_5$ [4] and Ce(Pd$_{1-x}$M$_x$)$_2$Al$_3$ [5] have been reported by means of simulating their respective inverse magnetic susceptibility-temperature curves.

Recently, Huo [4] and Im [5] have measured the magnetic susceptibility, magnetization and electrical resistivity of Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$, respectively. In this paper, we use the CEF program to simulate inverse magnetic susceptibility-temperature curves for Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$ in order to obtain CEF splitting levels. It is of interest to make an attempt to see some systematic behavior by comparing the same type compounds with different crystallographic structures.

2. Model and theory

We suppose the charge distribution of the surrounding environment is $\rho(R)$. Then electrostatic interaction potential between metal ion and i-valence electrons can be expressed by

$$V(\vec{r}) = \int \frac{\rho(\vec{R})}{|\vec{R} - \vec{r}|} d\vec{R}$$  \hspace{1cm} (1)

$\vec{R}$ and $\vec{r}$ denote the coordinate vectors of around ion and i-valence electrons, respectively.
The CEF Hamiltonian of rare ion is generally written as

$$H_{CEF} = -e \sum_i V(\vec{r}_i).$$  (2)

The summation includes all 4f electrons.

We can use the following formula

$$\frac{1}{|R - \vec{r}|} = \sum_{k=0}^{\infty} \frac{r^k}{R^{k+1}} P_k(\cos(\vec{R}, \vec{r}))$$  (3)

and

$$P_k(\cos(\vec{R}, \vec{r})) = \frac{4\pi}{2k+1} \sum_q (-1)^q Y_{kq}(\theta, \phi) Y_{k,-q}^*(\theta, \phi).$$  (4)

to obtain the concrete form of CEF Hamiltonian. Meanwhile, we also introduce tensor operator

$$C^k_q(\theta, \phi) = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}(\theta, \phi).$$  (5)

Here, $\theta$ and $\phi$ represent the polar angle and azimuth angle of $\vec{r}$ which characterize the position of 4f electron. $\theta$ and $\phi$ denote the polar angle and azimuth angle of $\vec{R}$ which characterizes the positions of surrounding ions.

Then, we can obtain the CEF Hamiltonian $H_{CEF}$ on the base of simple point-charge model with

$$H_{CEF} = \sum_{k,q} B^k_q C^k_q.$$  (6)

$B^k_q$ and $C^k_q$ are the CEF parameters and Stevens equivalent operators, respectively. The CEF Hamiltonian can be expressed as various polynomials of $B^k_q$ and $C^k_q$ within different symmetries.

Following the Hutchings notation, the CEF Hamiltonian for the orthogonal symmetry Ce$_2$NiGe$_6$ can be expressed in general form as

$$H_{CEF} = B^0_2 C^0_2 + B^2_2 C^2_2 + B^0_4 C^0_4 + B^2_4 C^2_4 + B^4_4 C^4_4.$$  (7)

The compound Ce$_2$NiGe$_3$ belongs to hexagon crystal system, only two nonzero CEF parameters are needed

$$H_{CEF} = B^0_2 C^0_2 + B^0_4 C^0_4.$$  (8)

In these Hamiltonians, $B^0_2$ coefficient is dominant since the others are smaller by an order of magnitude. The sixth order term is often neglected. The direction of the rare earth magnetic moment shows correlation with the sign of $B^0_2$ coefficient. For orthorhombic point symmetry, a negative sign of $B^0_2$ parameter implies that the magnetic moment aligns along the b-axis, whereas a positive sign is connected with the moment lying in the a-c plane, while for hexagon, a negative sign implies that the magnetic moments align along the hexagonal axis, a positive sign reveals that they are normal to it.

We next try a CEF analysis for a deeper understanding of this behaviour.

3. Results and discussion

It can be seen that the inverse magnetic susceptibility-temperature curves of Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$ in Refs. [4] and [5] significant deviate from Curie-Weiss law fits below 50 K, owing to that the strong
CEF effects which results in the splitting of the multiple ground states degeneracy for rare ion Ce$^{3+}$. And for this we calculate the eigen values and corresponding wave functions of Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$.

The first excited energy, total splitting energy and wave functions for Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$ derived from CEF calculation are listed in table 1. The analytical results of the CEF schemes show that the ground state for Kramers ion Ce$^{3+}$ is doublet. The six-fold degenerated ground state $^2\tilde{F}_{5/2}$ of orthogonal symmetry Ce$_2$NiGe$_6$ splits into three mixed doublets. The six-fold degenerated ground state $^2\tilde{F}_{5/2}$ of hexagon symmetry Ce$_2$NiGe$_3$ splits into three pure doublets. This is consistent with the Kramers law and the new wave functions are linear combinations of function with one J but different M in the presence of CEF. It is also worth mentioning that the difference of adjacent splitting energy in Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$ is rather small, meaning that the influences of Ge may be ignored, but the influences of different crystal system seem enormous [7, 8].

Figure 1 and Figure 2 show the calculated and experimental results of the inverse magnetic susceptibility for Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$, respectively. We can read off that the calculated magnetic susceptibility at higher temperature is consistent with the experiment results above 100K but the discrepancy becomes larger at lower temperatures, as shown in Figure 1 and Figure 2. There are mainly several possible reasons that may be leading to this discrepancy between the experiments and the calculation. First, we use isotropic field parameters in the calculation, but in fact there is a strong anisotropic effect especially in the case of low symmetry. Second, there is a strong hybridization between the f-electrons of the rare atoms and the d-electrons of the transition metal. Third, the appearance of spin glass freezing has caused the spin reorientation and fluctuation. Additionally, the other factors such as Kondo effect and RKKY interaction may have an influence on the magnetic moments [9, 10].

It is also worth mentioning that in some compounds CEF can change the magnetic ordering temperature in some compounds. Note that if we replace the simulation values of inverse magnetic susceptibility by magnetic susceptibility, then the discrepancy between CEF calculated and experiment data will become very small. Therefore, although the fitting of susceptibility gives only approximate values of splitting energies, the CEF calculation is rather reasonable within the experimental accuracy. In the case of Ce$_2$NiGe$_3$, the first excited energy 138K and overall splitting energy 496K coincides with 135K and 498K calculated by Huo [4] group through simulating the Schottky specific heat.

| Table 1. Eigen values E/K and corresponding wave functions of Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$. |
|---------------------------------------------------------------|
| **Eigen value** | **Wave function** |
|-----------------|-----------------|
| Ce$_2$NiGe$_6$  |
| 0               | $-0.04418|± 2.5\rangle + 0.65751|± 0.5\rangle + 0.75215|± 1.5\rangle$ |
| 78              | $0.11092|± 2.5\rangle + 0.75146|± 0.5\rangle - 0.65039|± 1.5\rangle$ |
| 557             | $0.99285|± 2.5\rangle - 0.05469|± 0.5\rangle + 0.10613|± 1.5\rangle$ |
| Ce$_2$NiGe$_3$  |
| 0               | $|± 0.5\rangle$ |
| 138             | $|± 2.5\rangle$ |
| 496             | $|± 0.5\rangle$ |
Figure 1. Temperature dependence of inverse magnetic susceptibility for Ce$_2$NiGe$_6$. Solid line shows the CEF calculated curve, and the open circles are the experiment curves.

Figure 2. Temperature dependence of inverse magnetic susceptibility for Ce$_2$NiGe$_3$.

4. Conclusions
We succeed in simulating the temperature dependence of inverse magnetic susceptibility for Ce$_2$NiGe$_6$ and Ce$_2$NiGe$_3$, and obtaining the CEF splitting levels and corresponding wave functions of Ce$^{3+}$. We analyze the influences of Ge content on CEF-scheme theoretically. Because of the complexity and sensitivity of magnetic susceptibility in the lower temperature, it is difficult to simulate exactly the lower temperature part. Therefore, the CEF calculated results give only approximate values of the splitting energies. The more exactly neutron scattering experiments are desired to determine the magnetic structure and confirm CEF splitting scheme.

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References

[1] Saha S R, Sugawara H, Matsuda T D, Aoki Y and Sato H 2000 Magnetic, thermal, and transport properties of single crystals of antiferromagnetic Kondo-lattice Ce$_2$PdSi$_3$ Phys Rev B 62 425-429

[2] Huo D, Skurai J, Kuwai T, Isikawa Y and Lu Q 2001 Electric, magnetic, and thermal properties of Ce$_2$NiGe$_3$: A Kondo lattice compound showing spin glass behavior Phys Rev B 64 224405

[3] Akamaru S, Isikawa Y and Sakurai J 2001 Magnetic properties and de Hass-van Alphen effect of PrNi$_2$Al$_3$ J Phys Soc Jpn 70 2049-2053

[4] Huo D, Sakurai J, Kuwai T, Mizushima T and Isikawa Y 2002 Antiferromagnetic in the Kondo lattice compound Ce$_2$Pd$_3$Si$_5$ Phys Rev B 65 144450

[5] Im H J, Min B H, Kwon Y S, Kim D L and H C Ri 2002 Magnetic and transport properties of the antiferromagnetic dense Kondo lattice system Ce$_2$Cu$_3$Ni$_{1-x}$Ge$_6$ Physica B 312-313 197-199

[6] Sun P, Lu Q, Kobayashi K, Kuwai T and Isikawa Y 2004 Schottky peaks in specific heat induced by electronic change in the antiferromagnetic-ferromagnetic alternating Kondo systems Ce(Pd$_{1-x}$M$_x$)$_2$Al$_3$ (m=Cu or Ag) Phys Rev B 70 174429

[7] Deng D and Li Y 2007 Theoretical calculation of Ce$^{3+}$ ground state for orthorhombic crystalline electric field Chin J Low Temp Phys 29 237-240 (in Chinese)

[8] Li Y, Du B, Wang H, Zhang X and Lu Q 2007 Theoretical calculation of crystalline electric field for rare earth compound CeRhGe and CeRhSn J At Mol Phys 24 40-44 (in Chinese)

[9] Tetsuya T, Arumugam T, Tomoyuki O, Mineko Y, Noriko, Takeshi Y, Yoshihiko I, Kiyohiro S, Andrei G, Etsuji K, Koichi K, Takao E and Yoshichika O 2003 Anisotropic, thermal, and magnetic Properties of CeAgSb$_2$: Explanation via a crystalline electric field scheme Phys Rev B 67 064403

[10] Tran V H 2004 Magnetic, electric transport and thermodynamic properties of Ce$_3$CuSn$_3$ J Alloy Compd 383 281