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UNUSUAL ANISOTROPY MECHANISM IN CE-PNICTIDES DUE TO VIRTUAL VALENCE FLUCTUATION

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Résumé.— La forte et inhabituelle anisotropie magnétique trouvée dans CeBi et CeSb est expliquée par un mélange anisotrope des états 4f et des électrons de valence. Ceci est compatible avec le fait qu'une telle anisotropie n'a pas été mise en évidence dans d'autres pnictures de cerium.

Abstract.--- Unusual strong magnetic anisotropies in CeBi and CeSb are explained based on the anisotropic mixing mechanism between the 4f states and the valence electrons. This is consistent with the fact that no such strong anisotropy is found in other Ce-pnictides.

Ce-pnictides are interesting materials showing various unusual anomalous properties. In CeN, Ce is believed to be tetravalency and thus non-magnetic /1/, while in CeP, Ce is trivalency and thus the real valence fluctuation is expected to occur in their alloys /2/. They are also interesting in the sense of narrow gap semiconductor. The gap between the conduction bands, which are made mostly by the 5d t_{2g} atomic states with the minimums at the three X-points /3/, and the valence bands, which are made mostly by the p states of pnictogens with a maximum at the Γ -point /3/, seems to disappear in between CeP and CeAs. In actual materials, however, because of the difficulty to make perfect crystals without vacancies, sharp change for the metal-non metal transition is not observed in their transport properties. On the other hand, the magnetic properties show a lot of variety /4/. In particular, the magnetic properties of CeSb and CeBi are very unusual, with many phases depending on temperature and magnetic field, however, in all of which the sublattice moments are kept in the [100] direction. Even the strong field up to 150 kOe in the [111] direction can not change the direction of the sublattice moments /5/. This is not understood from the usual crystal field effect because the ground state for the crystal field splitting is the doublet, which is spherical and in CeBi the crystal field splitting is believed to be very small.

Cooper tried to explain this unusual anisotropy by the strong magnetoelastic effect /6/, but it is difficult to give such a large anisotropy. Here, we explain this anisotropy on the stand point of the anisotropic f-p virtual mixing mechanism, or the anisotropic virtual valence fluctuating process.

In CeSb and CeBi, the 4f state is expected to be about 1 eV below the Fermi level. Therefore, in the first approximation, the 4f state in each Ce site is treated as a localized state under the cubic crystal field and the exchange field approximated by the usual molecular field form,

$$H_{4f} = \sum_i E_{4f} |SLJ v_i; i\rangle \langle SLJ v_i; i| \quad (1)$$

in which v_i means a 4f state in the above mentioned means in i-th Ce site. In this paper we show a simplest case, for simplicity, that is the perfect ferromagnetic alignment for $T=0$ and for the weak crystal field limit. More general case will be given in a separate paper. Therefore, in the following, $v_i = M_J$ in which the polar angles of the magnetic moment with respect to the crystal cubic axis are given by θ and ϕ .

As mentioned before /7/, the strongest mixing of the 4f state occurs with the valence p states because of the

shortest distance with pnictogens. Note that there are no intra atomic mixing between the 4f and the 5d bands. When the valence bands are filled, for CeN and CeP, no virtual f-p mixing effect exists except relatively small f-d mixing. Even in CeAs, in which the holes are expected to begin to be formed around the Γ -point, the f-p mixing effect seems to be not so important. In CeSb and CeBi, the number of the holes increases further and thus the f-p mixing effect should have important role. Here, the valence bands are treated by the simple tight binding model and then the f-p mixing matrix is given by the following form,

$$(sm_{s1}l_{m_1};i|V|SLJM_J;i') = \sum_{M_S M_L M_L'} (SM_S L M_L | JM_J) \times \exp[-i\phi(m_s + M_L)]$$

$$\times r_{SM_S}^{(s)}(\theta) r_{M_L M_L'}^{(L)}(\theta) \exp[-i\phi_{ii'}(m_l - M_L)]$$

$$\times r_{m_l M}^{(1)}(\theta_{ii'}) r_{M_L M}^{(L)}(\theta_{ii'}) (pfM) \quad (2)$$

in which the rotation matrices $r_{MM'}^{(J)}$ are given in, for example, Messiah's textbook /8/ and the Slater-Koster's integrals (pfM) are usually written as (pf0)=(pf σ), (pf1)=(pf π) and so on /9/. The polar angles of the lattice vector $R_{ii'}$ are given by $(\theta_{ii'}, \phi_{ii'})$ with respect to the crystal axis.

For simplicity, the f-p mixing is treated by the second order perturbation, even though it may not be a good approximation in the present case. The second order energy change U per Ce atom is given by

$$U = \sum_{\kappa\mu} \frac{|(\kappa\mu|V|JM_J;i)|^2}{E_{4f} - E_{\kappa\mu}} \quad (3)$$

in which the summations on κ and the band suffix μ are performed on the unoccupied valence bands and the valence band is given by the linear combination of the atomic p states, $|sm_{s1}l_{m_1}j_{m_j};i\rangle$. To see the situation clear, we treat here the two limiting cases. The case (i) is for the limit of the small hole number in which the holes are

concentrated at the Γ -point. The case (ii) is for the large hole number limit and we assume that the holes occupy the whole valence bands in an equal weight.

Case (i) We treat at first the weak ls coupling limit. Therefore the atomic state is given by $|m_{s1}m_l\rangle$. Then

$$U = \frac{n_h}{6(E_{4f} - E_{\Gamma_{15}})} \sum_{m_{s1}m_l} \left| \sum_i (m_{s1}m_l; i | V | M_J; 0) \right|^2 \quad (4)$$

in which n_h is the number of the valence hole per Ce atom. In the second, we treat the limiting case of the strong ls coupling and then the atomic state is given by $|m_{s1}m_l, j=\frac{3}{2}m_j\rangle$. Then

$$U = \frac{n_h}{6(E_{4f} - E_{\Gamma_{15}})} \sum_{m_j} \left| \sum_{i, m_{s1}} (j=\frac{3}{2}m_j | m_{s1}m_l) \times (m_{s1}m_l; i | V | M_J; 0) \right|^2 \quad (5)$$

The results for $s=S=1/2$, $l=1$, $L=3$ and $J=5/2$ are given in figure 1 for three directions of the magnetization, [001], [110] and [111] as functions of $(pf\pi)/(pf\sigma)$. Note that only the nearest neighbour mixing matrices are taken into account and then the simple symmetry argument requires that $-1 < (pf\pi)/(pf\sigma) < 0$. Therefore, in the first case, the easy direction is [110] and the hard direction [001] because of $E_{4f} - E_{\Gamma_{15}} < 0$ in disagreement with the experiment¹⁵. In the second case, too, the situation is similar to the first case as seen in figure 1.

Fig.1 Calculated energy shift U for case (i). Solid and broken curves show Eqs. (4) and (5), respectively.

Case (ii). U is approximated by

$$U = \frac{n_h}{6(E_{4f} - E_p)} \sum_{m_s m_l i} |(m_s m_l i | V | M_J; 0)|^2 \quad (6)$$

in which E_p is the average p band energy. The calculated results are shown in figure 2. Note that U is now a function of $|(pf_\pi)/(pf_\sigma)|$ and, for any value of it, $[001]$ is the easy direction in agreement with the experiment.

Fig. 2 Calculated energy shift U for case (ii)

For the estimation of the absolute value of U , the following values are chosen as reasonable values. $E_{4f} - E_p = -1$ eV, $(pf_\sigma) = 0.5$ eV and $n_h = 0.03/3$. Then the anisotropy energy is estimated to be $U[110] - U[001] \sim 4$ meV which corresponds to the external field of $H = \Delta U / g\mu_B (1 - \cos \pi/4) \sim 110$ T consistent with the observed large anisotropy.

The present mechanism may be understood in the following way. The 4f levels coexist with the valence bands and, through large f-p mixing matrix, make virtual bound states with fairly large width. When holes appear in the valence bands, the holes of the virtual bound states also appear, which, however, depend sensitively on the magnetic structure and temperature and thus induce

unusual magnetic properties. Strong anisotropy treated here is one of the unusual properties. Detail will be given in separate papers.

Similar phenomena seen in some actinide compounds seem to be the same origine.

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