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Valence Fluctuation in Sm$_3$Se$_4$

A. Ochiai, T. Suzuki and T. Kasuya

Department of Physics, Tohoku University, Sendai, Japan

Resume. - On a préparé un monocristal de Sm$_3$Se$_4$ et mesuré avec soin sa susceptibilité magnétique. Une analyse simple donne un résultat similaire à celui de Sm$_3$S$_4$ par Wachter. L'analyse par le modèle IBM comprenant l'interaction d'échange correspond aussi parfaitement aux résultats expérimentaux pour des valeurs raisonnables des constantes d'échange.

Abstract. - A single crystal of Sm$_3$Se$_4$ was prepared and the susceptibility was measured carefully. Simple analysis gives similar result to that of Sm$_3$S$_4$ by Wachter. Analysis by the IBM model including exchange interactions correctly also fits the data with reasonable values of exchange constants.

Sm$_3$X$_4$, in which X means chalcogen, are interesting materials in the sense that the Fermi level is just at the 4f level and Sm$^{++}$ and Sm$^{+++}$ coexist in the ratio 1:2 showing thermally induced valence fluctuating state. There is, however, big discrepancy in the understanding of the essential character of Sm$_3$S$_4$ between Zürich group and IBM group. The former showed that, after subtracting the susceptibility of Sm$^{++}$, the susceptibility of Sm$^{+++}$ indicates the doublet state to be lowest and disappearance of its moment above 50K /1/. One the other hand, disappearance of its moment above 50 K /1/. One the other hand, the latter claimed that the total susceptibility is well represented by the sum of Sm$_3$S$_4$, in which only Sm exists, and Sm$^{++}$, and there are no anomalies. Furthermore, they showed that the quartet should be lowest /2/. We made a fairly big single crystal of Sm$_3$Se$_4$ and examined the above problem more carefully both experimentally and theoretically.

The lattice constant was measured to be 8.880 Å and the molar susceptibility at room temperature is just in the middle of those of Sm$_3$S$_4$ and Sm$_3$Se$_4$ in IBM group /2/. These results indicate that our sample is good in the stoichiometry. The susceptibility was measured from 1.73K to 300K. Hereafter, we treat the value subtracted by the diamagnetic part of Se$^{--}$. AC resistivity was also measured, which will be reported in a separate paper.

At first, the similar treatment as Wachter is done. Susceptibility of Sm$^{+++}$, $\chi_3^T$, is estimated by subtracting that of Sm$^{+++}$, in which the singlet-triplet separation $\Delta$ is assumed to be 420K, which is the atomic value, and is 390K, which was used by Wachter /1/. Then, $\chi_3^T$ is plotted as a function of T in Figure 1. Compared with the values calculated by assuming that the quartet is situated 90K below the doublet as was proposed by IBM group /2/, discrepancy is clear. Instead of that, the data are well fitted by the model that the doublet is situated about 100K below the quartet. Furthermore, for $\Delta$=390K, $\chi_3^T$ behaves as if the localized moment is lost in part as Wachter found in Sm$_3$S$_4$. However, as the argument for the quartet lower seems to be correct from various other experiments /3/, we should try also to fit the data by the IBM model. The natural way is to include the exchange interaction, but the simple form does not fit the data as shown in figure 1. More careful treatment is necessary.

Here, we use the following form.

$$<s_2> = \chi_{sm2} h + \chi_{ss2} (J_{22}s_2 <s_2> + J_{23}s_3<s_3>)$$

and the similar formula for $<s_3>$ and $<s_3>$.

Where, $\chi_{sm2}=2\chi_{xx2}^T\chi_{xs2}$, $\chi_{ss2}$, for example means spin susceptibility of Sm$^{++}$ when an effective field acts only on spin of Sm$^{++}$, suffixes $\lambda$ and $m$ mean the orbital and the...
total moments, respectively, \( x_2 \) is the concentration of Sm++ and \( J_{22} \), for example, is the exchange interaction between Sm++. To make the calculation easier, we further used the following approximations for the exchange term. \( \chi_{bs2} = \chi_{bs3} = \chi_{mm2} \), in which the dominance of the singlet state is assumed and \( \chi_{mm2} \) is the usual Sm+++ susceptibility divided by \( \mu_B^2 \), and \( \chi_{bs3} = ((g_3-1)/g_3)\chi_{mm3} \), which means no exchange interaction with the van Vleck paramagnetic part of Sm+++ . Note that the above approximation causes no essential change in our final conclusion. Then, we have the following form:

\[
\chi_{mole} = \chi_2 + 2\chi_{3p} + 2\chi_{3v},
\]

(3)

\[
\chi_{2}^{-1} = \lambda_2 - J_{22}^* \frac{\lambda_2 - J_{22}^*}{\lambda_3 - J_{33}^*} J_{23},
\]

(4)

\[
\chi_{3p}^{-1} = \lambda_3 - J_{33}^* \frac{\lambda_3 - J_{33}^*}{\lambda_2 - J_{22}^*} J_{32},
\]

(5)

in which \( \chi_{3v} \) is the van Vleck term of Sm+++, \( \lambda_2^{-1} = \chi_{mm2} \), \( \lambda_3^{-1} = \chi_{mm3} \) excluding the van Vleck term, \( J_{22} = J_{22}^* \), \( J_{33} = J_{33}^* \). For \( \lambda_2^* \), the IBM model was used. Then, the best fitted values for exchange parameters are as follows. \( J_{22} = 15.7K, J_{33} = J_{33}^* = 20.2K, J_{32} = -6.2K \), and the result is shown in figure 2, both the total \( \chi \) including Se+++ and Sm++. Because \( \langle s_3 \rangle \) is antiparallel to \( \langle m_3 \rangle \) and large in the factor \( \alpha = 2.5 \), where \( g_3 = 2/7 \), the ferromagnetic coupling \( J_{32} \) causes \( \langle s_3 \rangle \) antiparallel to the applied field in lower temperature where \( \chi_{3p} \) becomes large rapidly. The small effective moment seen in figure 1 is understood in this way, in which \( J_{23} \) has essential importance.

Fig. 1 \( \chi_T \) obtained from our measurement by assuming \( \Delta = 420K \) and \( 390K \) for \( \chi_T \) are shown by \( * \) and \( . \). \( \chi_T \) calculated by using the IBM model without and with the exchange constant \( J_{33} = 6.2K \) are shown by the solid line and the dotted line.

This causes a question that why IBM group fitted their data by simple addition of \( \chi_3 \) and \( \chi_2 \) without exchange interaction between them. We tried to fit their data for Sm₂S₃ by using eq. (5) without the last term and found that it is difficult to fit them. More careful investigation of Sm₂S₃ is necessary. Note also that, as mentioned before, our data for SmSSe₄ is very similar to that of Sm₃S₄ by Wachter, even if we...
expect considerable change of exchange constants in sulphides and selenides.

Finally, the exchange mechanism are considered. The value of $J_{22}$ is about the same as those of SmS and EuO /4/. The same exchange mechanism, the mixed 5d electron aligns the spins on near neighbour Eu sites through the d-f exchange mechanism /5/, should be applicable. A larger value of $J_{23}$ is natural because the amplitude of 5d electron should be larger in Eu $^{++}$ than in Eu $^{+++}$, similar to a larger exchange constant of Eu-Gd doped in Eu- chalcogenides. A negative value of $J_{33}$ is expected because for Sm $^{+++}$ the mixing with the valence band should be important, in which negative spin polarization is induced in the valence electrons.

In conclusion, the susceptibility of Sm$_3$Se$_4$ can be interpreted both in the Wachter's model and in the IBM model with fairly large exchange interaction. In the latter case, the effect of the exchange interaction should be checked carefully.

References