THEORY OF DYNAMICAL JAHN-TELLER EFFECT ON MAGNETIC SUSCEPTIBILITY AND ITS APPLICATION TO UO2-ThO2 SYSTEM

K. Sasaki, Y. Obata

THEORY OF DYNAMICAL JAHN-TELLER EFFECT ON MAGNETIC SUSCEPTIBILITY AND ITS APPLICATION TO UO_2-ThO_2 SYSTEM

K. SASAKI and Y. OBATA

Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken, Japan

Résumé. — Les susceptibilités magnétiques du système UO_2-ThO_2, mesurées par Slowinski et Elliott et par Comly, sont analysées par le modèle simplifié du système vibronique. Dans ce modèle les ions paramagnétiques dans l'état triplet fondamental interagissent soit avec les modes tétragonaux localisés à une fréquence précise, soit avec ceux composés des phonons du type Debye. La susceptibilité est exprimée en fonction d'un facteur de réduction qui dépend de la température. Ce facteur réduit la constante de Curie effective et provoque une déviation par rapport à la loi de Curie-Weiss. L'accord avec l'expérience est satisfaisant.

Abstract. — The magnetic susceptibilities of UO_2-ThO_2 systems measured by Slowinski and Elliott and by Comly are analysed on the simplified models of vibronic system, where non-Kramers paramagnetic ions in triplet ground state interact either with localized tetragonal modes of vibration with sharp frequency, or with those composed of Debye phonons. The susceptibility is simply expressed in terms of a temperature dependent reduction factor which reduces the effective Curie constant and makes the susceptibility deviate from the Curie-Weiss law. Agreement with experiments is fairly good.

Uranium dioxide UO_2 and its diamagnetic isomorph, thorium dioxide ThO_2 have extensively been investigated to date on their electronic and magnetic properties. Recently Comly [1] measured the magnetic susceptibilities of the dilute solid solutions of UO_2 in ThO_2 in the temperature range between 1.7 °K and 60 °K, and has concluded that the smooth behavior of the magnetic susceptibilities at low temperature strongly suggests the triplet ground state. Interaction between the single-ion ground state and the lattice distortion is expected to be large in systems where ground state degeneracy is associated with the orbital state of the electrons (non-Kramers degeneracy). Solid solution of UO_2 in ThO_2 is a particularly interesting example of this situation. The electronic and magnetic properties of this system will be significantly modified by this orbit-lattice, or Jahn-Teller interaction. In this paper we briefly report the results of our analysis of the dynamical Jahn-Teller effect, the effect of the orbit-lattice interaction on the static magnetic susceptibility of UO_2-ThO_2 system [2].

We considered a magnetic U^{4+} ion surrounded by eight O^{2-} in the cubic coordination as in the solid solution of UO_2 in ThO_2. The ground electronic state was assumed to be a Γ_5 triplet derived from $5f^2$: $^3H_4$ multiplet. The non-Kramers paramagnetic ion interacts with tetragonal and trigonal modes of the XY_8 cluster which are shown in figure 1. The interaction with the trigonal modes is neglected for mathematical simplicity. As for the frequency spectrum of the tetragonal modes we adopted two models, localized and Debye. In the first model non-Kramers magnetic cation and its neighboring anions form a strongly coupled complex, more or less isolated from the other part of the crystal, and undergo localized or semi-localized vibrations well described by the tetragonal normal coordinates Q_2 and Q_3 of the XY_8 cluster, with frequency spectrum sharply distributed around ω. In the second model a non-Kramers cation interacts with the entire phonon spectrum in the crystal via the tetragonal coordinates Q_2 and Q_3.

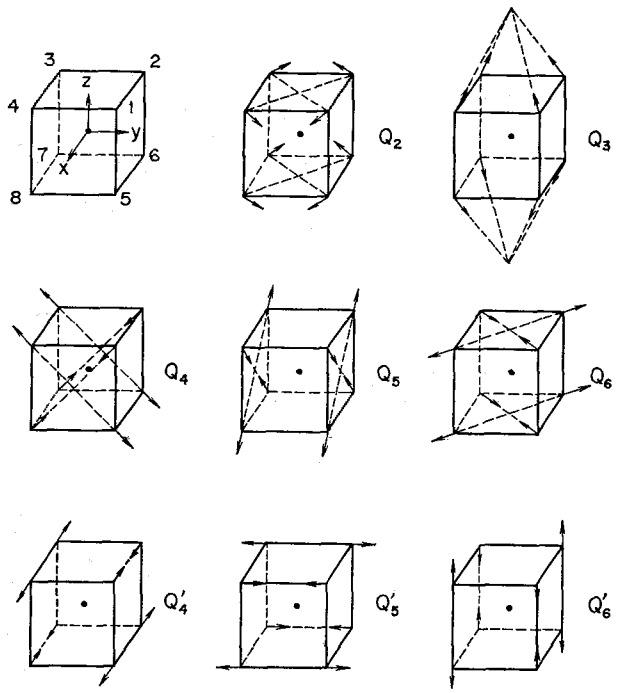

FIG. 1. — Normal modes of XY_8 cluster. Q_2 and Q_3 are the normal modes of tetragonal type vibrations. Q_4, Q_5, Q_6 and Q'_4,Q'_5,Q'_6 are of trigonal type respectively.

The susceptibility is simply expressed in terms of a temperature dependent reduction factor $\gamma_L(T)$ in the localized model, or $\gamma_D(T)$ in the Debye model, defined as the ratio of the susceptibility of a system with Jahn-Teller coupling to that of an ideal system without it : $\chi(T) = (C/T)\,\gamma_L(T)$, or $\chi(T) = (C/T)\,\gamma_D(T)$. We obtain-

ed the exact expressions for these reduction factors $\gamma_L(T)$ and $\gamma_D(T)$, as follows,

$$\gamma_L(T) = \int_0^1 dx \times \exp\left(-4G \frac{\sinh\left[\frac{T_\omega}{2T}x\right]\sinh\left[\frac{T_\omega}{2T}(1-x)\right]}{\sinh\left[\frac{T_\omega}{2T}\right]} \right),$$

$$\gamma_D(T) = \int_0^1 dx \times \exp\left(-8G \int_0^1 dy\, y \frac{\sinh\left[\frac{T_D}{2T}xy\right]\sinh\left[\frac{T_D}{2T}(1-x)y\right]}{\sinh\left[\frac{T_D}{2T}y\right]} \right),$$

where G is the Jahn-Teller coupling parameter; $T_\omega = \hbar\omega/k$; T_D the Debye temperature; and T is the absolute temperature of the system. Each of the reduction factors becomes, at 0 °K, equal to e^{-2G}, the square of the Ham's reduction factor [3] for an angular momentum operator, and asymptotically tends to unity as the temperature becomes infinitely high, making the susceptibility deviate from the well-known Curie-Weiss law, as shown in figure 2, where the solid curve is the $\gamma_L(T)$ computed with $G = 0.353$ and $T_\omega = 170$ °K, and as in figure 3 where the solid curve is the $\gamma_D(T)$ computed with $G = 0.353$ and $T_D = 263$ °K. In both figures the solid and the open circles correspond to the reduction factors deduced from Slowinski and Elliott's data for 9.3 % UO_2 in ThO_2 [4] and from Comly's for 9.2 % UO_2 [1], respectively. Both theoretical curves are pretty much the same, and are well matched with the experimental plot of the reduction factor, except at the lowest temperatures where magnetic ordering sets in. The values of the parameters determined are also reasonable. Figure 4 shows the temperature dependence of

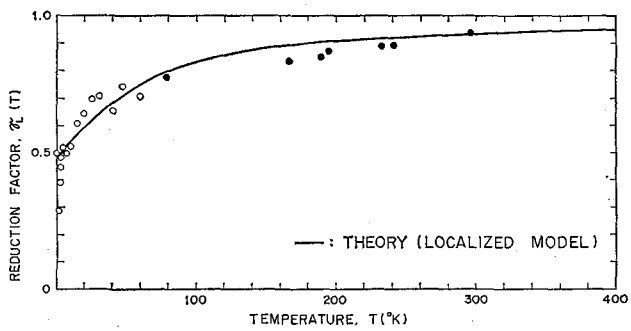

FIG. 2. — Temperature dependence of the reduction factor for the localized model of vibrational modes, $\gamma_L(T)$. o : the values obtained from Comly's data for 9.3 % UO_2 ;
● : the values from Slowinski and Elliott's data for 9.2 % UO_2 ;
—— : Theoretical curve with $G = 0.353$ and $T_\omega = 170$ °K.

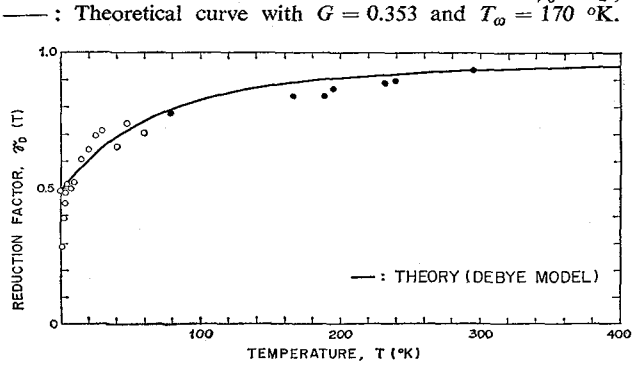

FIG. 3. — Temperature dependence of the reduction factor for the Debye model of vibrational modes, $\gamma_D(T)$.
o : the values obtained from Comly's data for 9.3 % UO_2 ;
● : the values from Slowinski and Elliott's data for 9.2 % UO_2 ;
—— : Theoretical curve with $G = 0.353$ and $T_D = 263$ °K.

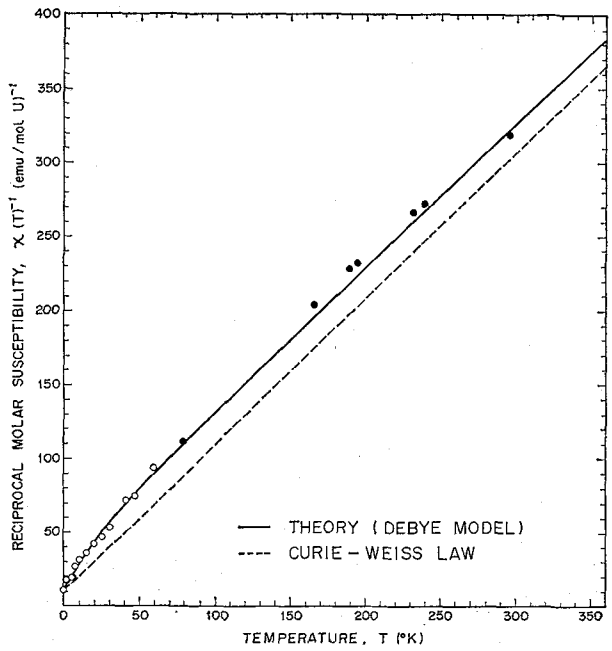

FIG. 4. — Temperature dependence of the reciprocal magnetic susceptibility of dilute solid solution of UO_2 in ThO_2.
o : Comly's data for 9.3 % UO_2 ;
● : Slowinski and Elliott's data for 9.2 % UO_2 ;
—— : theoretical curve for the Debye model with $G = 0.353$ and $T_D = 263$ °K ;
- - - : The Curie-Weiss law with Curie constant, $C = 1.02$ (e. m. u. degree/mol U) and molecular field constant, $\lambda = 11.48$ (e. m. u. /mol U)$^{-1}$.

the computed reciprocal susceptibility as well as the experimental data by Slowinski and Elliott, and by Comly. This shows that our theory based on the dynamical Jahn-Teller coupling well reproduces the convex curvature of the reciprocal susceptibility of UO_2-ThO_2 system. In general the agreement between the theory and the experiments is fairly good, although it should be taken with some reservations in view of the truncated nature of the Hamiltonian we used (*).

(*) Dr. F. S. Ham [5] has kindly pointed out to us that the present calculations can be adapted to the case of trigonal coupling by readjusting the coupling constants.

References

[1] COMLY (J. B.), *J. appl. Phys.*, 1968, **39**, 716.
[2] SASAKI (K.), OBATA (Y.), *J. Phys. Soc. Japan*, 1970, **28**, 1159.
[3] HAM (F. S.), *Phys. Rev.*, 1965, **138**, A1727.
[4] SLOWINSKI (E.), ELLIOTT (N.), *Acta cryst*, 1952, **5**, 768.
[5] HAM (F. S.), private communication.