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Synopsis

Experiments on the paramagnetic resonances of two nickel Tutton salts were performed at 47000 MC and at room temperature. The crystalline field constants were determined and compared with the results obtained by Griffiths and Owen on the same salts but at lower frequencies; for nickel ammonium salt, the result was in satisfactory agreement, but some differences between both the values were found in the case of nickel potassium salt. The crystalline field constants of the nickel potassium salt were found respectively to be $D = -3.50 \pm 0.01$ and $E = -5.55 \pm 0.01$.

I. Introduction

The phenomena of paramagnetic resonance absorption have been studied with the salts of various iron transition metals through various experimenters in accordance with the progress of the technique in microwave measurements. These experiments have made it clear that the method of microwave absorption is more direct in determining the ground state energy levels than the study of susceptibility and specific heat, etc.

Among various salts of iron transition metals, the salts of nickel have the spin triplet as its ground state, so this triplet state can be split by the appropriate crystalline electric field different from the case of cupric ion which has Kramers' degeneracy that cannot be removed by the crystalline electric field only.

Griffiths pointed out that⁽¹⁾ in the case of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, the crystalline electric field has rhombic symmetry and the triplet state splits completely, and the degree of splitting is 1.85 cm^{-1} and 0.77 cm^{-1} respectively. We performed the experiments on the microwave resonance absorption in $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and in $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ at 47000 MC at room temperature. We compared the crystalline field splitting of each salt in which the monovalent metallic ion was changed. During the course of the present study, Griffiths and his collaborators showed the various resonance data of nickel Tutton salts⁽²⁾. Comparing their results with ours which were derived at shorter wave length, satisfactory coincidence was seen between them except some differences in the case of nickel potassium salt.

II. Experimental procedure

The block diagram of apparatus is illustrated in Fig. 1. The microwave at the wavelength of 1.27 cm is generated by klystron 2K33 which is modulated by a saw

(1) J. H. E. Griffiths, & J. Owen, Proc. Phys. Soc. A **64** (1951), 583

(2) J. H. E. Griffiths, & J. Owen, Proc. Roy. Soc. **213** (1952), 459.

tooth wave of 150 C/S. The microwave of this frequency is multiplied by a crystal multiplier and its second harmonics ($\lambda = 6.35$ mm) was used for the present experiment. The cylindrical cavity which is coupled to TE_{11} mode was used and the sample was placed at the bottom of the cavity which is rotatable for the vari-

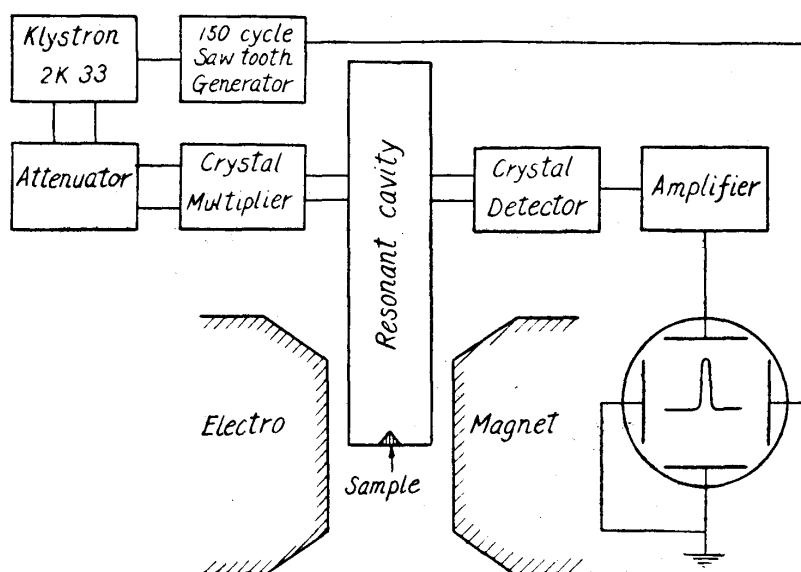


Fig. 1. The block diagram of the apparatus.

ation of the angle between the crystal axis and the external magnetic field. The magnetic field was applied with an electro-magnet which has the type of cyclotron and could make the uniform magnetic field of about 30 kilogauss when the pole gap was kept at 1 cm. The single crystal of nickel Tutton salts has been grown from the saturated aqueous solution in a thermostatt by natural evaporation. Its size is about 2 mm in diameter and the micro-photometer was used in determining the crystal surface and measuring the angle between the crystal axis and standard line marked on the cavity bottom when the crystal was mounted at the cavity. By this procedure, the precise correspondence of the absorption line and the crystal axis could be performed satisfactorily.

III. Crystallograph and energy levels of the nickel ion

$\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ are both belong to the so-called "Tutton salt". The compound generally has the standard formula $(\text{M}_I)\text{SO}_4 \cdot (\text{M}_{II})\text{SO}_4 \cdot 6\text{H}_2\text{O}$, where M_I denotes the monovalent metallic ion such as K, NH_4 etc, and M_{II} denotes the divalent metallic ions such as Cu, Ni and Zn, etc. Sometimes SO_4 group is replaced by SeO_4 group. The important character is that the salts of this group have almost the same crystal constant, and that we shall accordingly study on the effect of two different monovalent metallic ions from the crystalline field constants.

The X-ray analysis of nickel Tutton salt was carried out by Mukherjee⁽³⁾ who performed only the investigation of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. He found that the crystal constant is 8.98, 12.22, 6.10 Å and two nickel ions are placed in each unit cell and their positions are (0, 0, 0), $(\frac{1}{2}, \frac{1}{2}, 0)$ respectively and that this crystal belong to monoclinic and $\beta = 107^\circ 4'$. On the other hand, for the $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, β is determined to be $105^\circ 0'$.⁽⁴⁾ In both crystals, each nickel ion is surrounded

(3) P. L. Z. Mukherjee, *Kristallog.* **91** (1935), 504.

(4) P. Groth, *Chemische Kristallographie II Teil*, 521.

by six water molecules and the crystalline electric field is produced mainly by these water molecules.

For this crystalline electric field, Stevens and Griffiths⁽¹⁾ assumed the Hamiltonian as follows :

$$H = DS_z^2 + E(S_x^2 - S_y^2) + g\beta HS$$

From this Hamiltonian, we can get the energy level splitting of nickel ion by

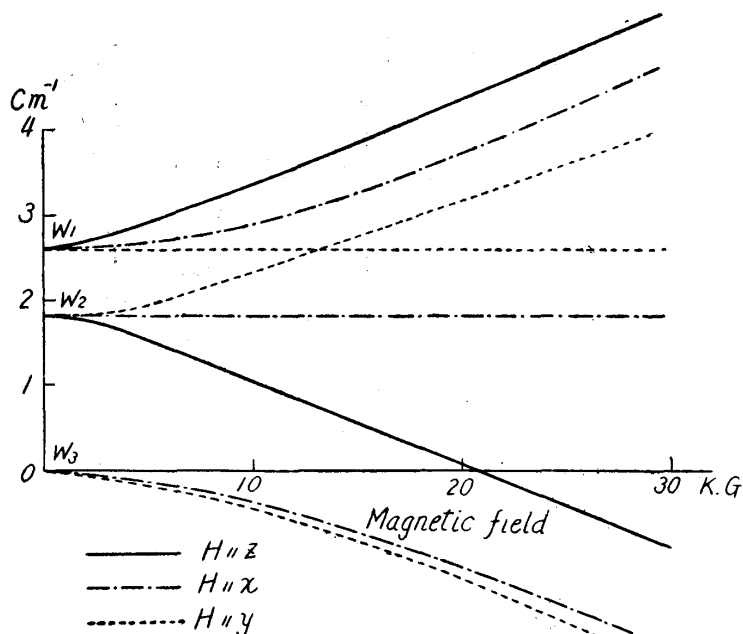


Fig. 2. The relative energy levels of nickel ion in $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

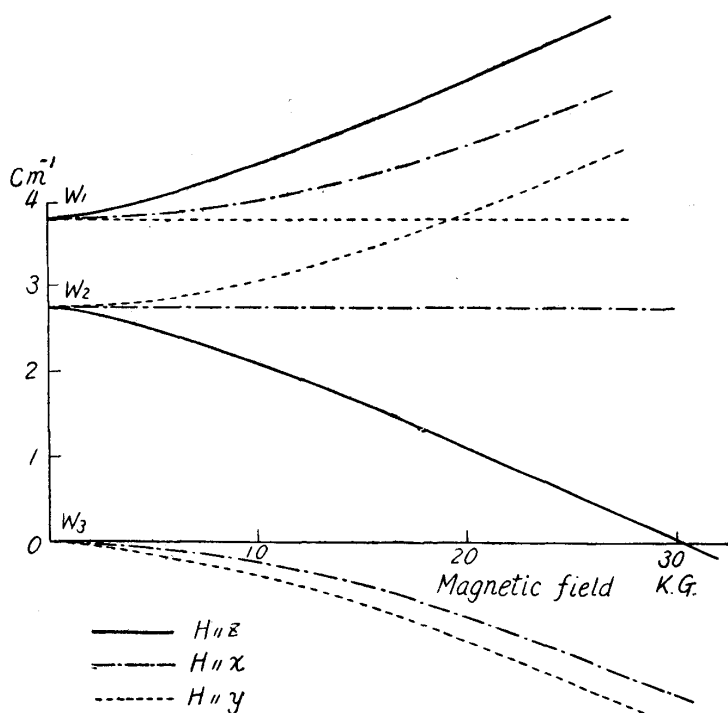


Fig. 3. The relative energy levels of nickel ion in $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

solving the secular equations. These results are illustrated in Fig. 2 and 3. For convenience, hereafter we call these levels W_1 , W_2 and W_3 according to the notation in Figs. 2 and 3. From these considerations we can get the splitting constants D , E and g by observing each resonance point in various directions, especially for the case that the external magnetic field is parallel to X, Y, Z axis respectively.

IV. Experimental results and discussion

As has been already mentioned, to determine the constants D , E and g , it is convenient to observe the resonance point when the external static magnetic field is parallel to X, Y, Z axis respectively. For this purpose, we considered two cases. One is the case of a-c plane parallel to the external magnetic field, and the other case is the magnetic field parallel to the plane which is perpendicular to the Z axis (hereafter we shall

call this X-Y plane). And the resonance point was plotted in rotating the magnetic field in this plane. From these data, we can determine D , E , g and ψ which is the angle of the crystalline c and Z axis, according to the notation given by Griffiths. Figs. 4 and 5 show the angular dependence of the resonance peak position for the $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ when a-c plane and X-Y plane are parallel to external magnetic field H respectively. In the case of a-c plane, we can see

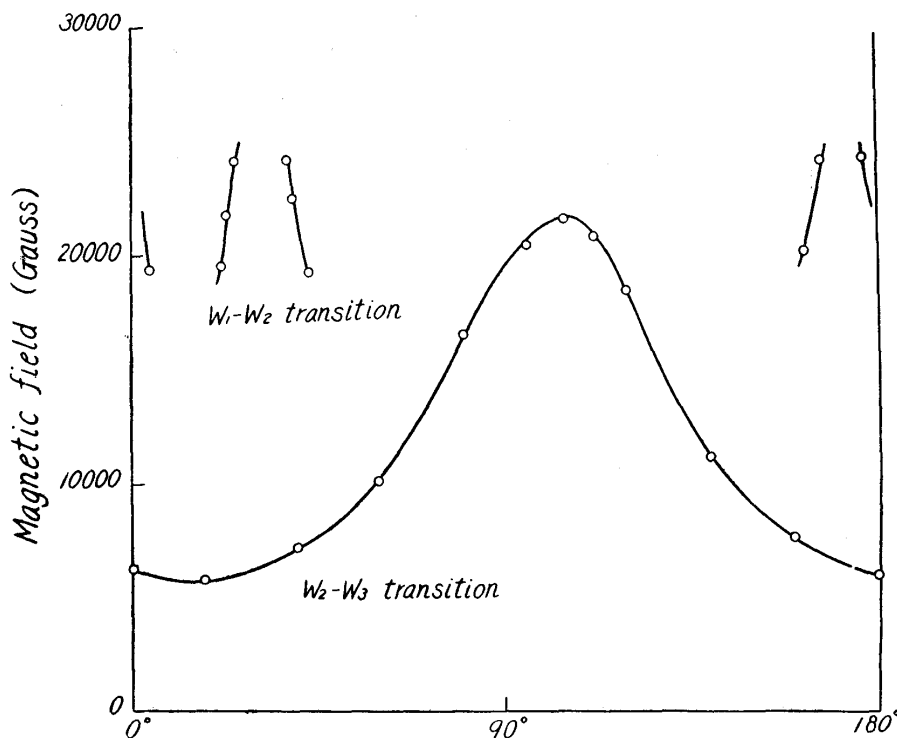


Fig. 4. The angular dependency of resonance point of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The external magnetic field is in the a-c plane and the abscissa shows the angle between the c axis and H . ($\lambda = 6.35$ mm).

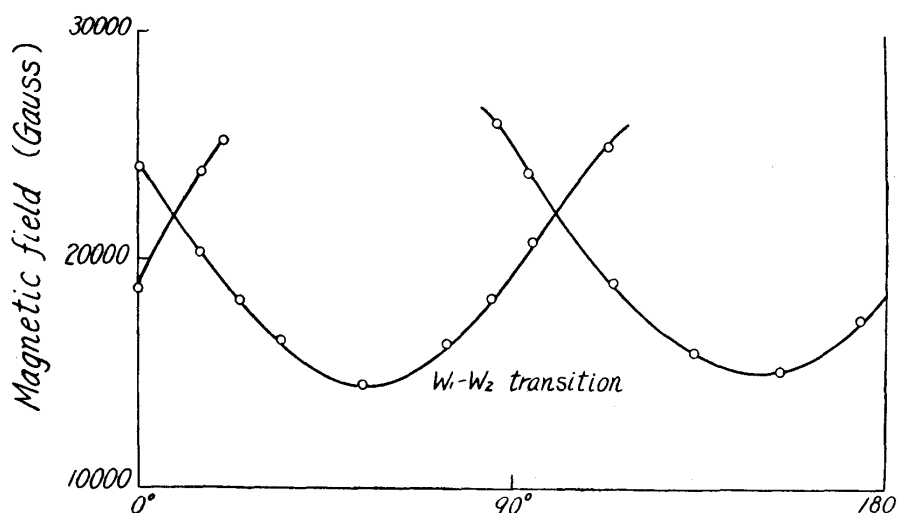


Fig. 5. The angular dependency of resonance point of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The external magnetic field is in the X-Y plane and the abscissa shows the angle between the direction to which the c axis is perpendicular and H . ($\lambda = 6.35$ mm).

the transition W_1-W_2 and W_2-W_3 but cannot separate the effect of two ions in the unit cell. In this case, we can determine only the transition energy of W_2-W_3 when $H//Z$. In other case where the magnetic field is parallel to the X - Y plane, however, two transition lines corresponding to the transition of W_1-W_2 were observed; this is resulted from two ions in the unit cell and from this data, we can determine the W_1-W_2 transition energy. From these results, we got the crystalline field constant as $D = -2.25 \pm 0.01$, $E = -0.39 \pm 0.01$ and they show very good coincidence with the Griffiths' data as shown in Fig. 6.

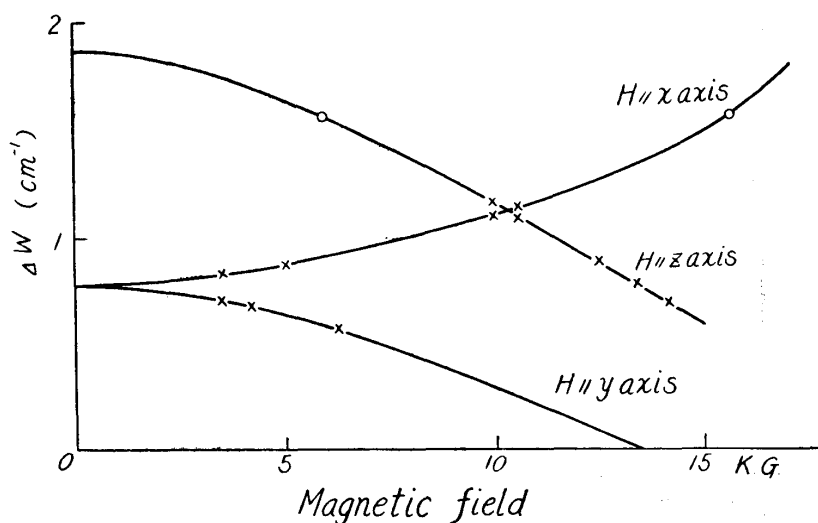


Fig. 6. The transition energy of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$; cross marks show the Griffiths' experimental results. Open circles denote the present experimental results.

Figs. 7 and 8 show the result of $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The result on X - Y plane is almost the same as that of the ammonium salt, but considerable difference was seen in the case of a - c plane. The partly lines observed at the high field side are W_2-W_3 transition line and the others are W_1-W_2 line. This W_1-W_2 line diminishes and could not be observed near the direction of $H//Z$, but we can estimate the resonance field when H is parallel to Z with considerable accuracy because of the behaviour of the resonance line as be shown in Figs. 7 and 8; from the above result, we can determine the crystalline field constant as $D = -3.50 \pm 0.01$, $E = -0.55 \pm 0.01$ and the result obtained shows some difference from the Griffiths data ($D = -3.30$, $E = -0.51$).

The result is summarized as follows: The experimental result at $\lambda = 6.35$ mm shows a good coincidence with the data of Griffiths who performed the experiment in the range $\lambda = 0.85$ cm~1.75 cm; the agreement of the angle of the crystalline axis with X - Y axis was also satisfactory. But in the case of $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, a slight difference with regards to the crystalline field constant was observed.

The cause of the difference of the crystalline electric field which was seen in these Tutton salts is not clear. The possible cause may be considered to be the change of the crystalline electron density or the change of the polarization of water molecules due to the difference of ion radius of K and NH_4 .

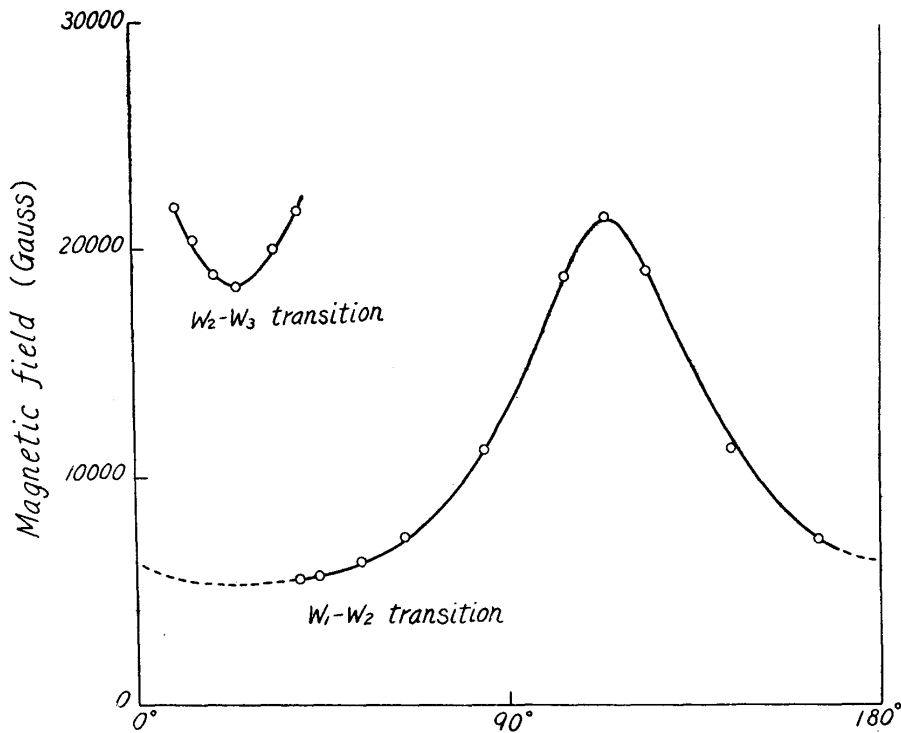


Fig. 7. The angular dependency of resonance point of $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The external magnetic field is in the a-c plane and the abscissa shows the angle between the c axis and H . ($\lambda = 6.35$ mm).

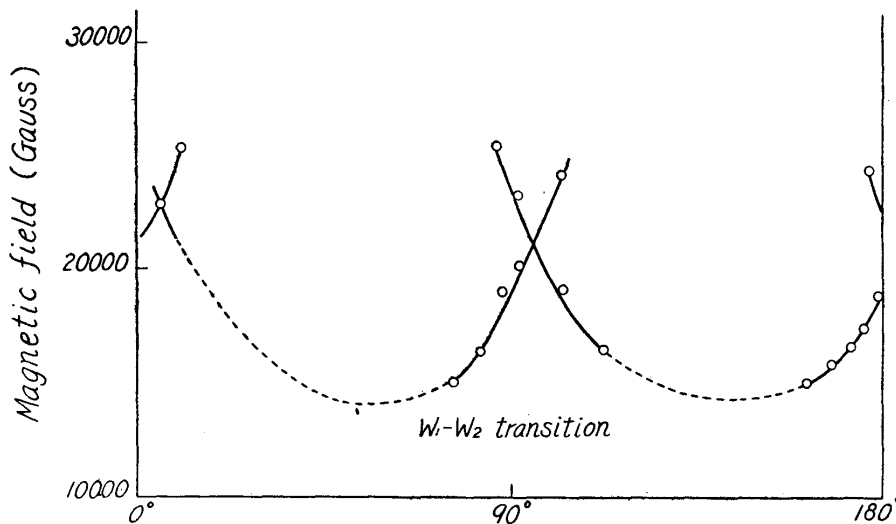


Fig. 8. The angular dependency of resonance point of $\text{NiK}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. The external magnetic field is in the x-y plane and the abscissa shows the angle between the direction to which the c axis is perpendicular and H . ($\lambda = 6.35$ mm).

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