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The Magnetic Anisotropy of Pyrrhotite and Iron Selenide

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The magnetocrystalline anisotropy in the *c*-plane of the crystals of the compound Fe_7S_8 and Fe_7Se_8 was studied by a torque magnetometer. It was found that in the range of strong field the torque amplitude at room temperature decreased with the inverse square of the field strength. The torque amplitude for Fe_7S_8 at liquid nitrogen temperature showed a maximum at a comparatively low field, but with further increase of the field strength the torque suddenly changed its sign; in a strong field range the torque amplitude reached the second maximum and decreased again. These facts are well explained by assuming a twin structure of the crystal.

The magneto-crystalline anisotropy in the basal plane of a crystal of the compound Fe_7Se_8* as well as Fe_7S_8** was investigated by a torque magnetometer. Figs. 1 and 2 show the relation between the torque value τ and the orientation of the magnetic field applied in the basal plane of a disc-formed crystal of the compound Fe_7Se_8. The torque amplitude of the six-fold Fourier component of the curve first increases with the magnetic field (Fig. 3), but with further increase of the field strength the amplitude begins to decrease. Fig. 4 shows the same

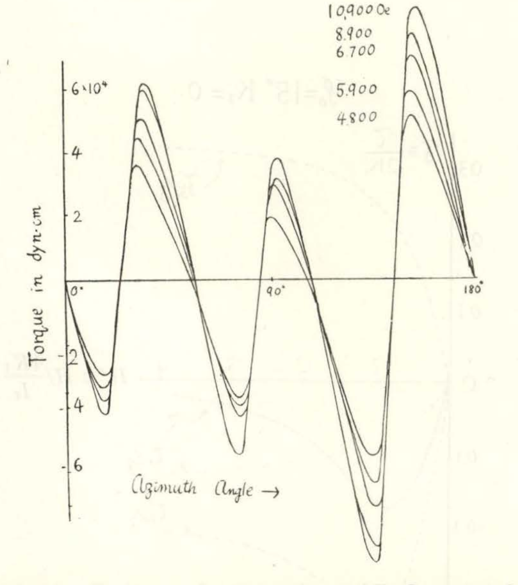

Fig. 1. Torque value in *c*-plane of Fe_7Se_8 crystal.

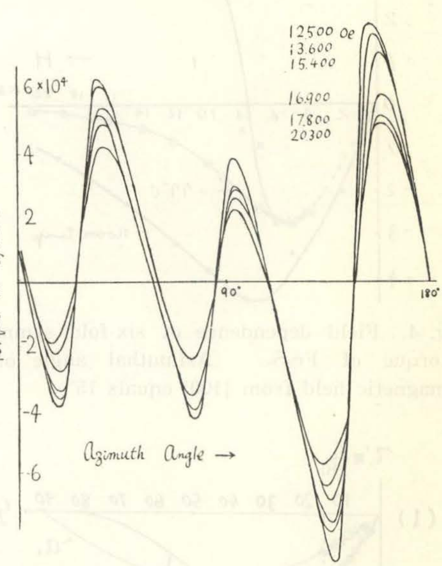

Fig. 2. Torque value in *c*-plane of Fe_7Se_8 crystal.

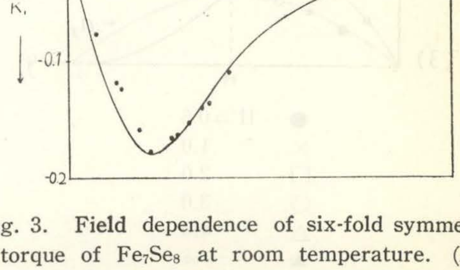

Fig. 3. Field dependence of six-fold symmetric torque of Fe_7Se_8 at room temperature. (Azimuthal angle of the magnetic field from [100] equals 15°)

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* The crystal was confirmed to have the 4c-structure.

** Natural crystal.

relation for the compound Fe_7S_8. The torque amplitude at room temperature decreases in proportion to the inverse square of applied magnetic field in the range of strong field intensity. But at the liquid nitrogen temperature the torque amplitude reaches its maximum at 6,000 Oe, then changes the sign, reaches the second maximum, and then decreases again.

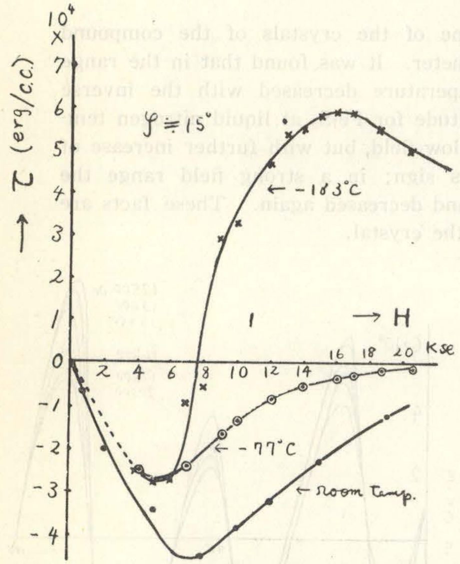

Fig. 4. Field dependence of six-fold symmetric torque of Fe_7S_8. (Azimuthal angle of the magnetic field from [100] equals 15°)

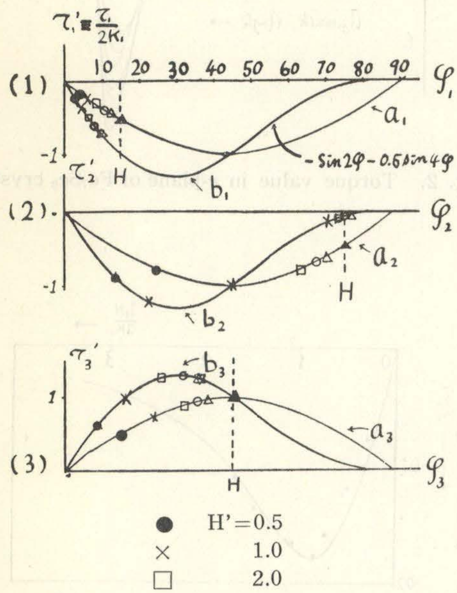

Fig. 5. Torque value from the crystal domains. The field direction $\psi=15°$

Now these facts can be theoretically understood by assuming a twin structure in the srystal of the Fe_7S_8[1] or Fe_7Se_8. The crystal lattice[2),3)] of these compounds was confirmed to have a monoclinic or triclinic deformation, then the crystal, which is thought to be hexagonal, is made up of three kinds of crystal domain with lower symmetry and each domain is uniaxially anisotropic in the direction [100], [010] or [$\bar{1}\bar{1}0$]: then these directions differ from each other by 120°. For each domain the crystal anisotrpy is expressed by

$$F=-K_1\cos 2\varphi_{1,2,3}.$$

Here φ's are azimuth angle of each magnetization. Then if a magnetic field is applied in a certain direction ψ in the c-plane, a sinusoidal torque occurs from each domain (as shown by curves a_1, a_2 or a_3 in Fig. 5). If the field strength is increased, a torque from each domain changes in the order ●, ×, □, ○, ,△··· as shown in Fig. 5, reaching ▲ at an infinitely strong field. Therefore as shown in Fig. 6, the resultant torque increases at first with the field but for very large field strength the resultant torque vanishes since

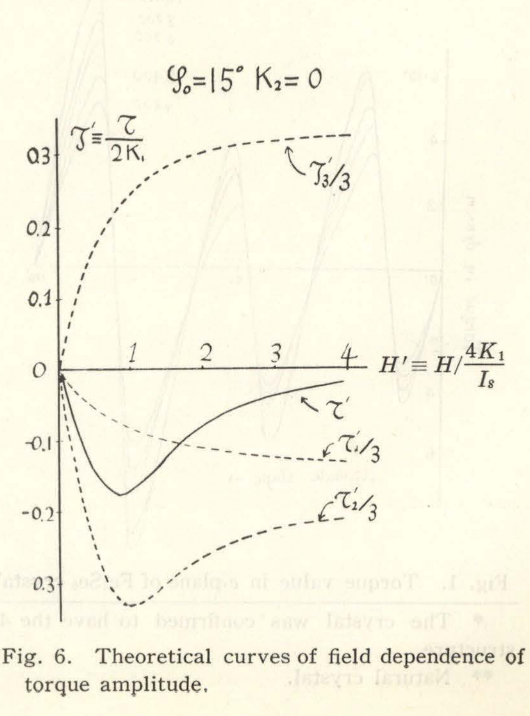

Fig. 6. Theoretical curves of field dependence of torque amplitude.

$$\sum_{n=0}^{2} \cos 2(\varphi+2n\pi/3)=0\ .$$

Based on this model, the field dependence of the torque amplitude can be well reproduced by choosing the constants as follows: $K_1=1.35\cdot10^5$ ergs/cc and saturation magnetization $I_s=44$ gauss, for Fe_7Se_8 and $K_1=1.41\cdot 10^5$ ergs/cc and $I_s=80$ gauss for Fe_7S_8.

Now if a higher order anisotropy, such as $-K_2\cos 4\varphi$, is added to the simple uniaxial anisotropy and F is expressed by

$$F=-K_1\cos 2\varphi-K_2\cos 4\varphi\ ,$$

then from this perturbation a deformation in the torque curve occurs as shown by the curve b_1, b_2 or b_3 in Fig. 5, resulting in a positive deviation in the case of K_1 and K_2 with the same sign. And if $K_2/K_1=1/4$ we can reproduce the observed behavior of the torque curve of sulphide at the liquid nitrogen temperature as shown in Fig. 7.

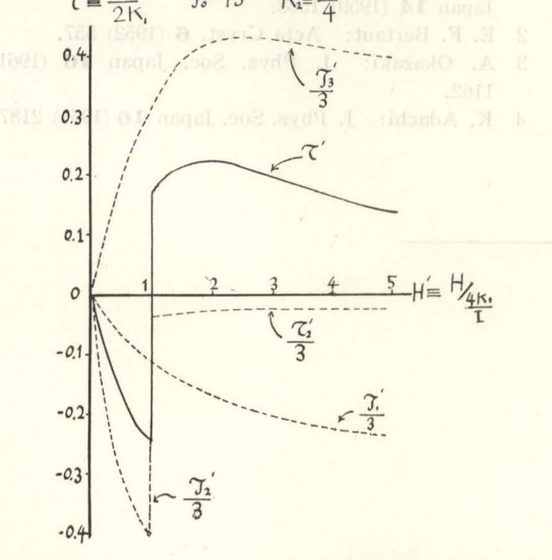

Fig. 7. Theoretical curves of field dependence of torque amplitude.

The origin of such anisotropy is considered to occur mainly from the spin-orbit interaction in the ferrous ion in the crystal lattice of these compounds. The crystals of the present compound contain, besides ferrous ions, a lot of vacancies as well as ferric ions in the metallic sites of the lattice and their arrangement is characterized by the model as shown in Fig. 8. In this case all the surrounding aspect of ferrous ions can be classified into three categories as shown in Fig. 9. (case a), b) and c)). The level scheme of ferrous ion ${}^5D$ shows a little change due

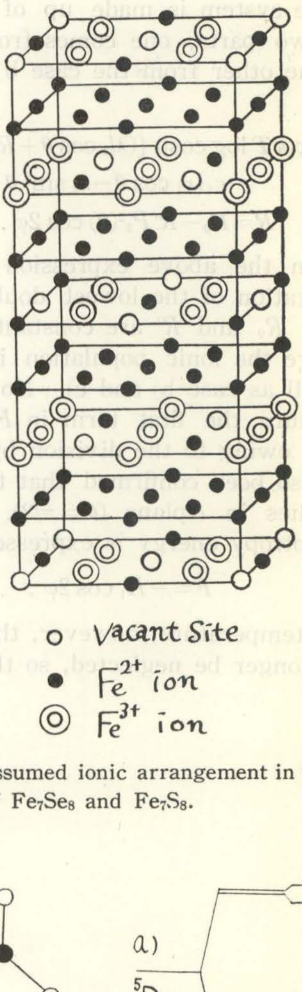

Fig. 8. Assumed ionic arrangement in the crystal lattice of Fe_7Se_8 and Fe_7S_8.

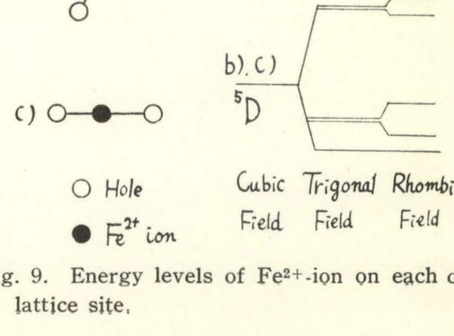

Fig. 9. Energy levels of Fe^{2+}-ion on each crystal lattice site.

to the crystal field[4]. A doublet level comes as the lowest in the case of a); in this case the orbital moment l_z is still living. While in the case b) or c) the lowest level is a singlet and in these cases the orbital moment is no longer living. So the free energy of the system is made up of quite different two parts, one comes from the case a) and the other from the case b) or c). We have

$$F=-c_1kT\log\cosh\{(\lambda l_z\cos\theta+R)/kT\}$$
$$-c_2\{\kappa_1\cos\theta-\kappa_2\sin^2\theta\cos2\varphi\}$$
$$R=R_0-R'P_2^2(\theta)\cos2\varphi\,.$$

$R(\theta,\varphi)$ in the above expression represents the separation of the lowest doublet in the case a). R_0 and R' are constants. Here c_1 and c_2 are the ionic population in the case a) as well as case b) and c). Now for high temperature the first term in F expression vanishes owing to the division by kT. And it has also been confirmed that the magnetization lies in c-plane ($\theta=\pi/2$). Therefore the anisotropy energy is expressed by

$$F=-K_1\cos2\varphi\,.$$

At low temperature, however, the first term can no longer be neglected, so that the anisotropy energy depends upon both θ and φ. The stable direction of spins deviated remarkably from the c-plane. If the magnetic field rotates in c-plane, then the magnetization also rotates following the field and the value of F changes during one cycle of rotation, resulting in apparent higher order anisotropy in c-plane. The calculated results are as follows.

$$F=-K_1\cos2\varphi-K_2\cos4\varphi\,,$$
$$K_1=-2(c_2\kappa_2\sin\theta_0-2c_1R')\,,$$
$$K_2=-(\kappa_2/\kappa_1)\sin\theta_0\cot\theta_0\,,$$
$$\cot\theta_0=(c_1\lambda l_z)/c_2\kappa_1\,.$$

Energy constants in the above expression can be semi-empirically determined. The theoretical value of K_1 as well as K_2 obtained in this way will be the correct order of magnitude for the observed anisotropy of these compounds.

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