Anisotropy of the cubic Fe_3S_4 induced in an electrostatic field

Abstract. A synthetic iron sulphide of spinel type became anisotropic when immersed in an electrostatic field. Analysis of the electron diffraction patterns observed from the Fe_3S_4 specimens showed that a preferred induction took place at about 313 K along the [111] axis in the crystal. This anisotropy became negligibly small over about 373 K.

An aqueous suspension of synthetic iron sulphide (Fe_3S_4, space group: Fd3m, spinel structure, $a_0 = 9{\cdot}87$ Å) was smeared on a smooth surface of mica lamina, about $3 \times 3 \times 0{\cdot}1$ mm³ in size. The thickness of the sulphide layer deposited was about one micron. The specimen was then investigated in terms of electron diffraction. The disposition of the experiment is illustrated in figure 1. A monoenergetic electron beam served for charging up the specimen with electrons (Yamaguchi 1966), for heating it by means of electron bombardment (Yamaguchi 1962), and for carrying out the diffraction experiments (Yamaguchi 1968).

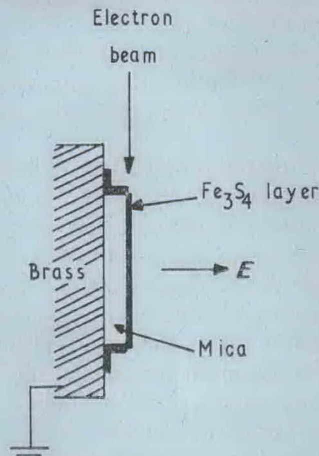

Figure 1. This shows the Fe_3S_4 layer deposited on a mica surface. A monoenergetic electron beam plays three roles, to charge up the mica layer, to heat the sulphide film and to undergo diffraction at it. $\boldsymbol{E}$ is the electrostatic field.

The diffraction patterns observed are shown in figures 2 and 3,which correspond to the

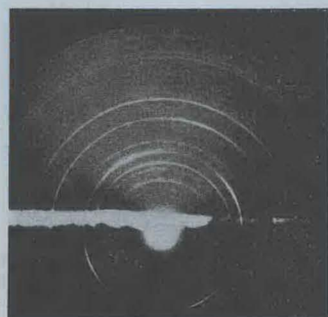

Figure 2. This shows the diffraction pattern from the sulphide specimen in figure 1. At a temperature of about 313 K. The reference pattern of gold is superimposed on the specimen pattern, and the (333) reflection from the sulphide shows a preferred displacement. Wavelength of the electrons: 0·0440 Å (75 kV), camera length: 50 cm.

Also included in the figures are the theoretically calculated values of Horner (1970), who used a L–J potential and summed ladder diagrams to all orders to produce src, and the results of experiments.

From the results several conclusions and comments can be made. Although ΔF changes the SCP ground state energy considerably (see figure 1) it produces very little change in the volume derivatives of the free energy (the SCP pressure and compressibility are not shown in figures 2 and 3 as their difference between the ISC values is so small that their inclusion would only detract from the clarity of the graphs). The pressure and compressibility are in relatively good agreement with experiment. We found that the compressibility curve calculated in this work lay virtually on top of the ^{3}He curve that was calculated in I using the L–J potential. For this reason that curve is not reproduced here. The SCP ground state energy is far too high. ΔF is of the right sign and magnitude to lower the energy and produce a value closer to Horner's (1970) result. It must be noted, however, that since ΔF is large compared with F_{sc} (nearly half its value at 18 cm^3) the original philosophy of ISC of treating it like a perturbation on the SCP free energy is questionable. The contribution of the next to the leading term of the second order theory, involving the fourth order force constant squared, might also be substantial. It is interesting to note, however, that this term is also likely to contribute a negative energy and lower the ISC ground state energy even more.

The use of the soft core Beck potential removed the computational difficulties involved in the hard core L–J potential calculations. Accurate numerical results could be obtained over the full volume range considered without recourse to src. Nevertheless the deep penetration of the SCP Gaussian wavefunction into the core of the repulsive part of the helium potential is physically unrealistic, and, we believe, is one of the major reasons for the very high value obtained for the ground state energy using SCP. SCP theories that include src (see for example Koehler 1967) lower the ground state energy considerably. These theories clearly contain greater anharmonicities than are involved in SCP alone and this is illustrated somewhat in the present work where higher order anharmonic terms have been included in SCP within the framework of ISC.

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