THE MAGNETIC PROPERTIES OF IRON-PYRITES

By S. Ramaseshan

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

Received January 20, 1947

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The magnetic susceptibility of iron-pyrites (FeS_2) has been determined by various workers and widely different results have been reported. Recent studies on this substance by Sigamony (1944) have shown that the mass susceptibility values range from $0 \cdot 2 \times 10^{-6}$ to 190×10^{-6}, although a majority of the crystals tend to have values near about the lower limit. It was, therefore, thought that the study of the magnetic properties of a large number of crystals and an attempt to correlate the magnetic properties with other physical properties would be of considerable interest.

From the large stock of crystals in the possession of Sir C. V. Raman, 105 perfect crystals were selected. All the crystals, excepting one which was a twin, were approximately cubic in form having a bright metallic lustre. The crystals were all tin-white in colour.

2. Variation of Susceptibility with Specimen

An approximate determination of the susceptibility of each of the 105 crystals was made by observing the deflection produced in a Curie balance. The values of the mass susceptibility varied from $0 \cdot 2 \times 10^{-6}$ to 300×10^{-6}. Of the 105 crystals, 95 had values between $0 \cdot 2 \times 10^{-6}$ to $0 \cdot 7 \times 10^{-6}$, seven between $2 \cdot 5 \times 10^{-6}$ to 40×10^{-6} and three between 100×10^{-6} to 300×10^{-6}. Of these, 16 crystals having no flaws or imperfections were selected and accurate determinations of the mass susceptibility were made. For crystals having low susceptibilities Rabi's null method was used with a dilute solution of $MnCl_2$ as the bath. The crystal was suspended in the non-homogeneous field from one arm of a Curie balance of low torsional constant. Any deviation from the null point when the field was put on, could be very sensitively detected by a lamp and scale arrangement. It was found that in all cases the susceptibility was higher at a lower field. The crystals were usually saturated for fields above 5000 gauss, and the baths were adjusted for exact balance for fields greater than this. The value of mass susceptibility of crystals 3, 40, 105 and 17 were found by comparison with very strong solutions of manganous chloride. The value for crystal No. 17 is only approximate. The susceptibility values of the 16 crystals are given in Table I.

TABLE I

Crystal No.	5	9	6	1	2	7
$\chi \times 10^6$	0·206	0·219	0·236	0·247	0·312	0·333
Crystal No.	4	8	16	18	33	35
$\chi \times 10^6$	0·356	0·391	0·492	0·503	0·530	0·627
Crystal No.	3	40	105	17		
$\chi \times 10^6$	2·43	28·9	187	280		

The field dependence of susceptibility of 7 crystals were determined and the results are given in Table II.

TABLE II

Crystal No.	$\chi \times 10^6$ 2900 gauss	$\chi \times 10^6$ 3700 gauss	$\chi \times 10^6$ 4500 gauss	$\chi \times 10^6$ 5400 gauss
5	0·224	0·210	0·206	0·206
6	0·263	0·244	0·236	0·236
7	0·351	0·340	0·334	0·333
35	0·671	0·639	0·628	0·627
3	..	2·97	2·50	2·43
40	..	34·5	29·8	28·9
17	..	365	289	..

The dependence of susceptibility on temperature was investigated for two crystals having low susceptibility values. The usual Curie balance method was employed. A heater with its coils non-inductively wound was used. The temperature was measured to an accuracy of one degree with a copper constantan thermocouple. It was found that if crystals were heated above 200° C. and cooled, the susceptibility values before and after heating differed slightly. The susceptibility of crystals increased from $0{\cdot}206 \times 10^{-6}$ to $0{\cdot}215 \times 10^{-6}$. This increase was absent when crystals were heated to 170° C. Table III gives the variation of mass susceptibility with temperature at different field strengths.

TABLE III

Crystal No.	Temperature	Susceptibility $\chi \times 10^6$		
		2900 gauss	3700 gauss	4500 gauss
1	25°	0·267	0·255	0·247
	65°	0·252	0·251	0·237
	92°	0·250	0·236	0·220
	122°	0·247	0·230	0·218
	163°	0·245	0·228	0·218
2	26°	0·339	0·326	0·312
	61°	0·329	0·319	0·302
	87°	0·323	0·312	0·295
	115°	0·317	0·307	0·290
	144°	0·315	0·305	0·285

All the 10 crystals having higher susceptibilities were tested for remanent magnetism. The periods of oscillation in the earth's magnetic field before and after the crystals were magnetised in a strong magnetic field (17000 gauss) were determined. The periods were the same within 0·005% indicating that there was practically no remanent magnetism. The crystals having high susceptibility (No. 17 and No. 105) were found to be slightly anisotropic.

3. CHEMICAL ANALYSIS

An estimation of the sulphur content of some typical crystals was made by chemical analysis. The method adopted is the one advocated by Hillebrand (1929). FeS_2 is oxidised by a solution of bromine in CCl_4 and HNO_3 to $FeSO_4$. The sulphur is precipitated out as B SO_4 and weighed. An accuracy of 0·5% could only be achieved. Table IV gives the sulphur content of some of the crystals.

TABLE IV

Crystal No.	Sulphur%			$\chi \times 10^6$
	Determination I	Determination II	Mean	
2	53·57	53·40	53·48	0·312
5	53·42	53·37	53·40	0·206
7	53·62	53·38	53·50	0·332
66	53·42	53·22	53·32	20·0

The results indicate that there are some stochiometric variations in sulphur content but the evidence is not conclusive owing to the inaccuracies in the determination. It must be mentioned here that there was some insoluble component (most probably silica) in each of the crystals, the amount of this component being never more than 0·4%.

4. SPECIFIC GRAVITY DETERMINATION

As the chemical analysis was not very conclusive, a systematic determination of the specific gravity was undertaken. Each crystal was suspended from the arm of a chemical balance by means of a very fine quartz fibre. The weight of the crystal in air and in distilled water (25° C.) were determined from which the specific gravity was calculated. Table V and Fig. 1 give the specific gravity and magnetic susceptibility of 12 typical crystals. It is estimated that the error in the specific gravity determination could not be more than 2 or 3 units in the 3rd place of decimal. The letter (A) indicates the values of susceptibility that have been determined only approximately.

TABLE V

Crystal No.	Specific Gravity	$\chi \times 10^6$
1	5·001	0·247
4	4·997	0·356
10	4·995	0·230
8	4·990	0·391
3	4·992	2·43
103	4·980	7 (A)
91	4·973	15·0 (A)
66	4·982	20·0 (A)
40	4·970	28·9
45	4·943	139 (A)
105	4·930	187
17	4·919	289

5. DISCUSSION OF RESULTS

The density of pure FeS_2 has been observed (1912, 1932) to be between 5·00 and 5·02 which is higher than the values of density of the different crystals used in this investigation. It will be noticed from Table V that the magnetic susceptibility is higher for crystals having lower densities. This precludes the possibility of the paramagnetic susceptibility arising out of iron as impurity; for in that case the density should increase with susceptibility. The lower values of the density could only be due to the absence of atoms of iron or sulphur or both from the lattice of iron-pyrites. The magnetic data, however, seem to favour the idea that the number of atoms of sulphur absent from the structure is more than twice the number of atoms of iron absent. In such a case the Fe : S ratio would be greater than 1 : 2, In this connection the work of Juza and Blitz (1932) is of great interest. These workers have prepared a series of compounds of the formula FeS_n, n having values between 1 and 2, by heating pure iron pyrites under different conditions of temperature and pressure. The results of their studies on the X-ray structure, magnetic susceptibility and density of these substances are summarised in Table VI. The results of X-ray and magnetic investigations are particularly interesting. Compounds lying between FeS and $FeS_{1 \cdot 12}$ have the hexagonal crystal structure of Pyrrhotite, while those between $FeS_{1 \cdot 90}$ and FeS_2 have the cubic structure of iron-pyrites. Compounds having formulæ between $FeS_{1 \cdot 12}$ and $FeS_{1 \cdot 90}$ are composed of a mixture of FeS and FeS_2. The magnetic behaviour of these compounds is given in Fig. 2. The susceptibility gradually increases from $0 \cdot 4 \times 10^{-6}$ to 5500×10^{-6} as the iron: sulphur ratio decreases, but it drops to a very low value when the composition corresponds to $FeS_{1 \cdot 1}$. The curve given in Fig. 1 corresponds approximately to the part of the curve in Fig. 2 enclosed within dotted lines. As only very few observations of density and susceptibility of compounds having composition very near FeS_2 have been made by Juza and Blitz, no comparison can be made between their results and those obtained in the present work. But a study of Tables V and VI and Figs. 1 and Fig. 2 shows clearly that the phenomenon observed in natural crystals of iron-pyrites

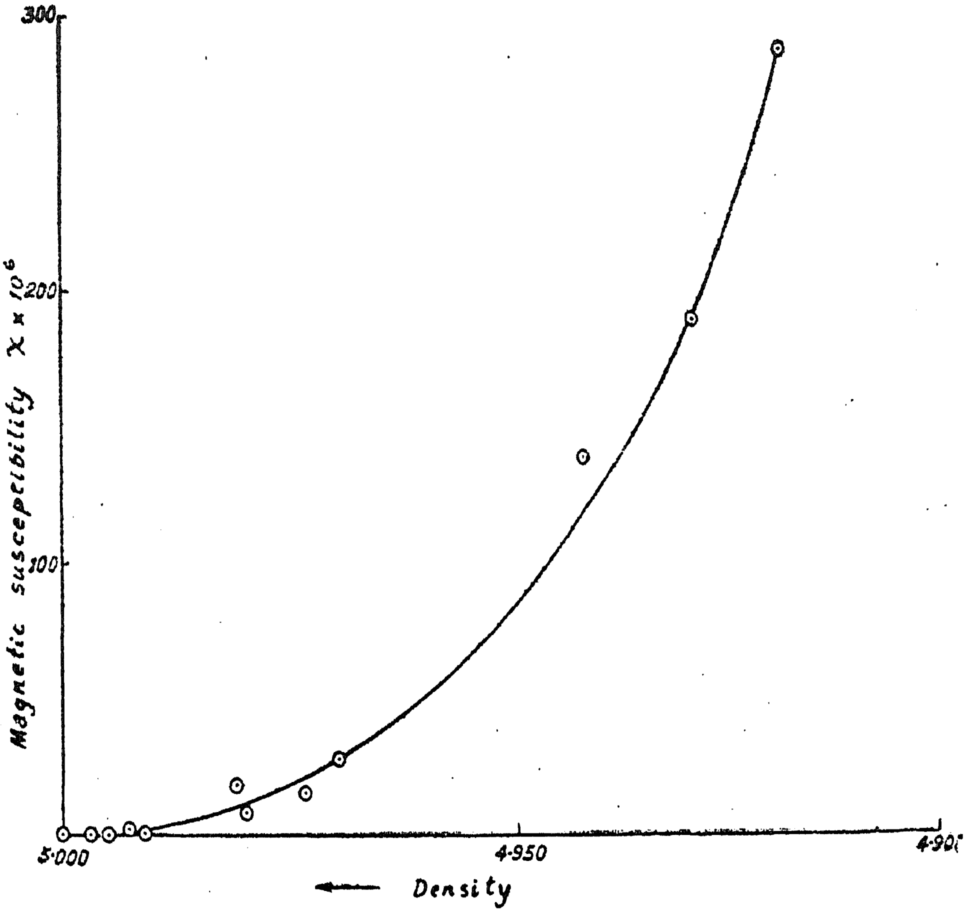

FIG. 1. Variation of magnetic susceptibility with density

TABLE VI

Preparation	FeS_n $n =$	X-ray structure	Density	Mol. Vol.	$\chi \times 10^6$
1	1·942	FeS_2	4·978	23·7	0·45
2	1·907	FeS_2	4·975	23·5	283
3	1·720	FeS_2+FeS	4·894	22·7	1220
4	1·450	FeS_2+FeS	4·769	21·4	3180
5	1·345	FeS_2+FeS	4·725	20·9	4170
6	1·187	FeS_2+FeS	4·605	20·4	4930
7	1·118	FeS	4·593	19·95	5590
8	1·060	FeS	4·637	19·4	94·2
9	1·026	FeS	4·736	18·2	14·2

observed in this investigation is generally analogous to that observed by Juza and Blitz in artificially produced sulphides of iron. It may be mentioned here that the slight anisotropy observed in crystals having higher susceptibility may be due to the presence of hexagonal FeS in cubic FeS_2.

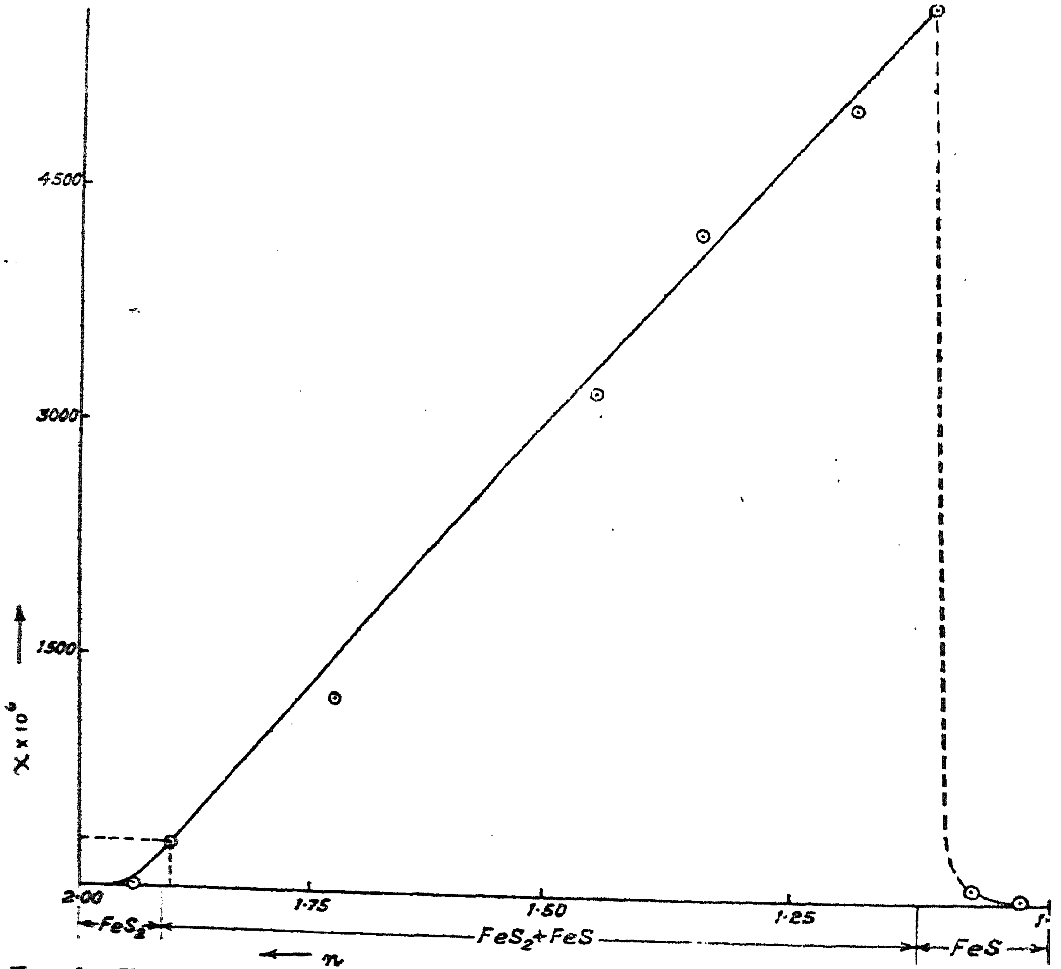

FIG. 2. Variations of magnetic susceptibility with composition (Juza & Blitz)

It is easy to qualitatively understand the appearance of paramagnetism due to the absence of sulphur atoms in the FeS_2 lattice. In the iron-pyrites structure each iron atom is octahedrally surrounded by six sulphur atoms and each sulphur atom tetrahedrally by three iron and one sulphur atom. If the small residual paramagnetism of FeS_2 ($0\cdot2 \times 10^{-6}$) be neglected, one could consider all the spins of the electrons in the Fe—S and S—S bonds to be completely compensated. The removal of one sulphur atom from the FeS_2 structure results in the uncompensation of the spins in three Fe—S and one S—S bond giving rise to paramagnetism. It is hardly likely however that this elementary consideration would be sufficient to explain the high susceptibility values obtained by Juza and Blitz. Approximate computations show that while calculated and observed values are of the same order when the Fe : S ratio is nearly 1 : 2, they are widely different as the ratio increases.

In conclusion, the author wishes to thank Professor Sir C. V. Raman for the loan of the crystals of iron-pyrites and for the keen interest he took during the course of this investigation.

6. SUMMARY

Determination of the magnetic susceptibility of 105 crystals of iron-pyrites have been made and it is found that 95 crystals have values between $0\cdot2 \times 10^{-6}$ to $0\cdot7 \times 10^{-6}$, seven between $2\cdot5 \times 10^{-6}$ and 40×10^{-6} and three between 100×10^{-6} and 300×10^{-6}. A definite correlation between susceptibility and density has been established, crystals with higher susceptibility having lower density. The lowering of the density may be attributed to the absence of iron and sulphur atoms from the crystal lattice. If the number of sulphur atoms missing from the lattice is much greater than the number of iron atoms thus increasing the iron : sulphur ratio, the magnetic data obtained with natural crystals of iron-pyrites in this investigation would be analogous to those obtained by Juza and Blitz with artificially prepared compounds of iron and sulphur having compositions intermediate between FeS_2 and FeS.

REFERENCES

Allen, E. T., Crensham, J. L., and Johnson, J. .. *Amer. Jour. Sc.*, (4), 1912, **33**, 169.

Dana .. *A System of Mineralogy.*

Hillebrand .. *Applied Inorganic Analysis*, Wiley & Sons, 1929.

Jackson, L. C. .. *Nature*, 1929, **123**, 219.

Juza, R., and Blitz, W. .. *Zeit. anorg. Chem.*, 1932, **305**, 273.

Mellor .. *A Treatise on Inorganic Chemistry.*

Pauling, L., and Huggins, M. L. .. *Zeit. Krist.*, 1934, **87**, 205.

Sigamony, A. .. *Proc. Ind. Acad. Sci.*, 1944, **20A**, 204