Temperature-dependent magnetic susceptibility of marcasite (FeS$_2$)

Mohindar S. Seehra and M. S. Jagadeesh

Physics Department, West Virginia University, Morgantown, West Virginia 26506

(Received 29 May 1979)

The magnetic susceptibility χ of a natural sample of marcasite (FeS$_2$) has been measured with a Faraday balance in the temperature range 4.2–380 K. For $T < 150$ K, the data follow the expression $10^6\chi = 64 + (787/T)$ cm^3/mole, where the Curie-type contribution is from a magnetic impurity. For $T > 180$ K, χ increases weakly with increasing T. The estimated χ for pure marcasite varies from 64×10^{-6} cm^3/mole at 4.2 K to 68×10^{-6} cm^3/mole at 380 K. The observations suggest a low-spin configuration for Fe^{2+} in marcasite leading to Van Vleck paramagnetism, similar to the case of iron pyrite. Some details of the Faraday balance used in these studies are also given.

I. INTRODUCTION

The transition-metal dichalcogenides have been the focus of considerable attention in recent years since their magnetic and electrical properties depend strongly on the transition-metal constituent.[1-3] Recently we have reported on the magnetic,[4] optical,[5] and dielectric properties[6] of iron pyrite (FeS$_2$). A detailed study of the transport properties of iron pyrite (hereafter referred to as pyrite) has been reported by Horita and Suzuki.[7] In summary these studies have shown that pyrite is a Van Vleck paramagnet (Fe^{2+} is in the low-spin configuration) and a semiconductor. An indirect band gap of about 0.84 eV in the limit of 0 K has been reported.[5]

The mineral marcasite has the same chemical formula (viz., FeS$_2$) as pyrite. However, they have different crystal structures; whereas pyrite has a modified NaCl-type structure with $a = 5.42$ Å, marcasite is orthorhombic with $a = 4.45$, $b = 5.42$, and $c = 3.39$ Å.[8] Consequently some differences in the various physical properties of marcasite and pyrite might be expected. The Mössbauer studies of Temperley and Lefevre[9] have indeed shown some differences in the Mössbauer parameters (quadrupole splittings and line shifts) of marcasite and pyrite. Hulliger and Mooser[10] have summarized some of the earlier studies in the marcasite structure compounds.

In this paper we report a detailed study of the magnetic properties of marcasite using magnetic susceptibility (χ) as a probe. The only other known magnetic susceptibility study in marcasite has been that of Serres.[11] However, this study was limited to the region above room temperature (293–460 K) and we present arguments later in this paper that these susceptibilities were dominated by contributions from magnetic impurities. In the present work we have measured the magnetic susceptibility of a comparatively pure natural sample of marcasite in the temperature range of 4.2–380 K. From this study we

infer that Fe^{2+} ion in marcasite is in the low-spin configuration (posseses no moment in the ground state), resulting in Van Vleck paramagnetism, somewhat similar to the situation in pyrite.[4] Some relevant details of the Faraday balance used in these studies to measure χ are also given.

II. EXPERIMENTAL DETAILS

The magnetic susceptibilities have been measured by the Faraday method using a Cahn RG electrobalance in conjunction with the Lewis gradient coils.[12] Many systems employing the Faraday method and the RG balance have been described in the literature.[13] However, a major advance in this technique was achieved by Lewis[14] by the use of the gradient coils instead of the tapered pole caps to produce the nonuniform field. This allowed control of the field gradient independent of the magnetic field, provided a uniform field gradient over about a cm height, and provided an output proportional to the magnetization, among other advantages.[14] Except for the variable temperature probe, our system is quite similar to that described by Lewis.[14] In our system, the output of the balance is fed to a Keithley Model 155 amplifier, the output of which is recorded on a x-y recorder (Hewlett Packard Model 7044A). A Janis Dewar is used for operation in the range 4.2–400 K. The different temperatures are obtained by a heater wound over a brass portion (near the sample zone) of a stainless-steel hangdown tube. The temperatures can be stabilized to within $\frac{1}{10}$ degree using an Artronix Model 3501E temperature controller and monitored with thermocouples (Cu-Au/Fe for $T < 50$ K and Cu-Constantan for $T > 50$ K) in conjunction with a potentiometer (Keithley Model K4). The thermocouples are placed in close proximity to the sample and temperatures are stabilized for about 8–10 minutes at each temperature before data are taken. The sensi-

tivity of this system is about 5×10^{-7} emu for mag-
netic moment measurements and a magnetic field up
to 10 kOe is available from a Varian 9 inch magnet.
The balance was standarized against a Pd standard
obtained from the National Bureau of Standards
(NBS).

Although a quartz fiber is the most commonly
used hangdown wire, we have found cotton thread to
be equally acceptable. As sample containers, Pt boats
(supplied by Cahn Instruments Inc.) and Al sheets
(99.95 purity, supplied by Ventron Inc.) were used.
For measurements of very small X as reported here,
Al is preferred as a boat material because it gives
considerably lower background than the Pt boat be-
cause of its lower X and lower density. In Fig. 1 we
have plotted X for Pt and Al versus T. Duco cement,
which was used as a glue with the Pt boat for
powdered materials, slightly lowers its X due to di-
amagnetic contribution. (Results of Fig. 1 are
presented partly as an aid for others using the Fara-
day technique). Our X for Pt boat at room tempera-
ture is within 1% of the value provided by the NBS
for a Pt standard, thus attesting to the purity of the
boat material. For Al sheets X values at room tem-
perature are about 10% higher than the NBS stan-
dard. This and the rise in susceptibility of the Al
sheet at lower temperature is indicative of the contri-
butions from impurities. Nevertheless, the back-
ground deflection of Al for a 64 mg marcasite sample
at room temperature was only 9% compared to about
60% for the Pt boat. Consequently Al was used as
the boat material in this work. For other details of a
modern Faraday apparatus, see Refs. 13 and 14.

The sample used in these studies was natural crys-
tal obtained through the courtesy of the Morgantown
Energy and Technology Center of the Department of
Energy. The sample, silvery in appearance, was x-ray

analyzed. This analysis unambiguously showed the
marcasite structure and absence of pyrite.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The magnetic susceptibility of the marcasite sam-
ple, measured in a magnetic field of 10 kOe and in
the temperature range of 4.2–380 K, is shown in Fig.
2 (open circles). Note that the measured susceptibili-
ty is minimum near about 180 K with increases for
$T > 180$ K considerably smaller than those for
$T < 180$ K. In many respects, this behavior is similar
to the observation in pyrite, where an increase in X at
lower temperatures was attributed to the presence of
impurities since at these temperatures different sam-
ples yielded different susceptibilities which were
found to be proportional to the levels of magnetic im-
purities.[4] Assuming a similar situation in the case of
marcasite, we interpret the measured X as a sum of
contribution from the magnetic impurities and a con-
tribution from the intrinsic susceptibility of marcasite.
Analysis of the data shows that for $T < 150$ K, the
data can be described quite well by the equation

$$10^6 X = 64 + (787/T),   \tag{1}$$

as shown in Fig. 2. Equation (1) assumes a
temperature-independent susceptibiltity for marcasite
$(64 \times 10^{-6}$ cm^3/mole) below 150 K and the contribu-
tion of the impurities to vary as the Curie law. The
Curie constant of Eq. (1) is consistent with an impur-
ity level of 0.05 at.% with a magnetic moment
$\mu = 3.5\mu_B$ or an impurity level of 0.1 at.% with
$\mu = 2.5\mu_B$. These levels of impurity are difficult to
detect with x-ray analysis and chemical methods
could not be tried because of their destructive nature
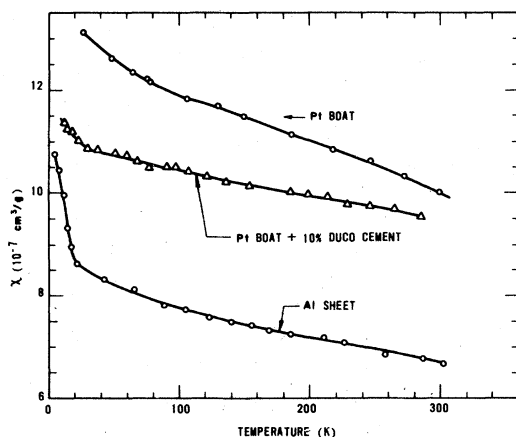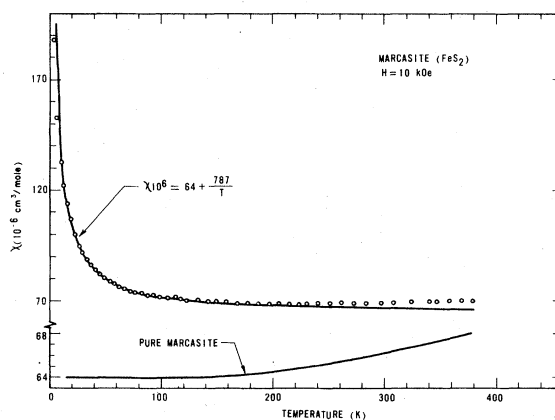and since only a small amount of sample was avail-

FIG. 1. Magnetic susceptibility of some sample holders as a
function of temperature. To correct for this background,
magnetization of a sample holder is subtracted from the
magnetization of a sample of given mass at a given H.

FIG. 2. Measured susceptibility (open circles) of the mar-
casite sample vs temperature. The upper solid curve is Eq.
(1) and the lower solid curve (with a change in the scale of
ordinate) is the estimated variation of X for pure marcasite.

able. However these numbers (impurity levels and magnetic moments) are comparable to the analysis of the best pyrite sample discussed in Ref. 4. Some iron group impurities are likely to be present in marcasite as in the case of pyrite.[4]

The difference between Eq. (1) and the measured χ for $T > 150$ K is interpreted to be due to the temperature dependence of χ for pure marcasite. This estimated temperature dependence is also shown in Fig. 2 (bottom curve). Note that this interpretation successfully explains the minimum in χ vs T observed near 180 K for marcasite.

Using the above interpretation, the observation of Serres[11] who measured χ for a marcasite sample in the range 293–460 K is easily understood. The susceptibility was observed to decrease with increasing temperatures, the reported values being 156×10^{-6} cm^3/mole at 293 K and 145×10^{-6} cm^3/mole at 458.7 K. Compared to our observations, these values are over a factor of 2 higher and have the opposite temperature dependence. Both the larger magnitudes and Curie-type behavior of χ observed by Serres in 293–460 K range are indicative of significantly larger amount of impurities present in the sample. Since χ for pure marcasite is quite small and it is only weakly temperature dependent, it is quite understandable that even small amounts of impurities can dominate the behavior of magnetic susceptibility.

Now we consider the magnetic susceptibility of pure marcasite (Fig. 2). It is noted χ vs T behavior for marcasite is qualitatively similar to the observations in pyrite.[4] The small value of χ and its temperature dependence are consistent with the interpretation of Fe^{2+} being in the low-spin state, quite similar to the case in pyrite.[4] Consequently, an analysis of the data could be carried out in a fashion similar to that oulined in Refs. 4 and 15. In particular we note that in such a case, the total $\chi = \chi_{vv} + \chi_d$, where χ_{vv} and χ_d are, respectively, the Van Vleck and diamagnetic (negative) contributions. It follows that in marcasite $\chi_{vv} > |\chi_d|$. Also, since χ_d is expected to be temperature independent and χ_{vv} to vary nearly as the inverse of the energy band gap E_g,[4] the observed increase of χ for pure marcasite with increasing temperatures is consistent with E_g decreasing with increasing temperatures, a phenomenon observed in most semiconductors including pyrite.[5] Above about room temperature, where the Curie-type contribution of the impurities to the susceptibilities of marcasite and pyrite are negligible, we note that χ for marcasite is about three times larger than that for pyrite. A calculation of χ for marcasite, for comparison with the experiment, can be carried out[4,15] if the band structure of marcasite is known. However, to the best of our knowledge, an estimate of E_g or a calculation of the band structure of marcasite is not available at present.

ACKNOWLEDGMENTS

[1]J. A. Wilson and A. D. Yoffe, Adv. Phys. 18, 193 (1969), and references therein.

[2]E. K. Li, K. H. Johnson, D. E. Eastman, and J. L. Freeouf, Phys. Rev. Lett. 32, 470 (1974).

[3]A. D. Mabatah, E. J. Yoffa, P. C. Eklund, M. S. Dresselhaus, and D. Adler, Phys. Rev. Lett. 39, 494 (1977).

[4]P. Burgardt and M. S. Seehra, Solid State Commun. 22, 153 (1977); P. A. Montano and M. S. Seehra, ibid. 20, 897 (1976).

[5]W. W. Kou and M. S. Seehra, Phys. Rev. B 18, 7062 (1978); M. S. Seehra and S. S. Seehra, ibid. 19, 6620 (1979).

[6]D. E. Husk and M. S. Seehra, Solid State Commun. 27, 1147 (1978); also, D. E. Husk, M. S. thesis (West Virginia University, 1978) (unpublished).

[7]H. Horita and T. Suzuki, Sci. Rep. Res. Inst. Tohoku Univ. 25, 124 (1975).

[8]M. J. Buerger, Am. Mineral. 16, 361 (1931). For an up-date see C. S. Hurlbut, Jr. and C. Klein, Manual of Mineralogy, 19th ed. (Wiley, New York, 1977); and G. Brostigen et al., Acta Chem. Scand. 27, 2791 (1973).

[9]A. A. Temperley and H. W. Lefevre, J. Phys. Chem. Solids 27, 85 (1966).

[10]F. Hulliger and E. Mooser, J. Phys. Chem. Solids 26, 429 (1965).

[11]A. Serres, J. Phys. Rad. 14, 689 (1953).

[12]R. T. Lewis, Rev. Sci. Instrum. 42, 31 (1971).

[13]B. L. Morris and A. Wold, Rev. Sci. Instrum. 39, 1937 (1968); R. K. Quinn and R. C. Knauer, ibid. 43, 1543 (1972); A. N. Gerritsen and D. H. Damon, ibid. 33, 301 (1962); B. Dellby and H. E. Ekström, J. Phys. E 4, 342 (1971).

[14]R. T. Lewis, J. Vac. Sci. Technol. 11, 404 (1974). A system based on the Lewis design is available from George Associates Berkeley, California.

[15]L. A. Marusak, C. Cordero-Montalvo, and L. N. Muley, Mater. Res. Bull. 12, 1009 (1977).