the use of the conjecture regarding the effects of the magnetic field on the two energy gaps is

$$\alpha_L = \frac{\pi N_s m_s v_{sF}}{6\rho_{\text{ion}} v_s^2}\,\omega_S \left\{1 - \frac{4}{\pi^{3/2}}\,\frac{\Delta_s}{\epsilon_s} \times \left[K(k) - \frac{1}{3}\left(\frac{\pi T}{\epsilon_s}\right)^2 (K(k) + k\,K'(k)) + \cdots\right]\right\}$$

$$+ \frac{\pi N_d m_d v_{dF}}{6\rho_{\text{ion}} v_S^2}\,\omega_S \left\{1 - \frac{4}{\pi^{3/2}}\,\frac{\Delta_d}{\epsilon_d} \times \left[K(k) - \frac{1}{3}\left(\frac{\pi T}{\epsilon_d}\right)^2 (K(k) + k\,K'(k)) + \cdots\right]\right\}, \quad (27)$$

where the definitions of all the terms are found in Ref. 1.

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[1]I-M. Tang, Phys. Rev. B 2, 2581 (1970). There is an error in this paper which can be rectified by putting a band subscript on the y parameter in Eq. (3.5).

[2]K. Maki, Phys. Rev. 156, 437 (1967).

[3]I-M. Cyrot and K. Maki, Phys. Rev. 156, 433 (1967).

[4]U. Brandt, W. Pesch, and I. Tewordt, Z. Physik 201, 209 (1967).

[5]D. R. Tilley, Proc. Phys. Soc. (London) 84, 573 (1964).

[6]L. P. Kadanoff and I. I. Fal'ko, Phys. Rev. 136, A1170 (1964).

[7]See K. Maki, in *Treaties on Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

[8]J. W. Hafstrom and M. L. A. MacVicar, Phys. Rev. B 2, 4511 (1970).

[9]J. R. Carlson and C. B. Satterthwaite, Phys. Rev. Letters 24, 461 (1970).

[10]H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Letters 3, 552 (1959).

[11]N. Tsuda and T. Suzuki, J. Phys. Chem. Solids 28, 2487 (1967).

[12]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[13]H. C. Wu, H. V. Bohm, and R. L. Thomas, Phys. Rev. B 2, 122 (1970). The multiple gaps in pure mercury and lead superconductors are believed to arise from pair correlation in the higher Brillouin zones in the crystals. This multigap effect is somewhat different from the multigap nature of the transition-metal (TM) superconductors [the multiple gaps in the TM are related to the overlapping s-p and d (f) bands found in these metals].

[14]J. E. Randorff and B. J. Marshall, Phys. Rev. B 2, 100 (1970).

[15]R. W. Morse, IBM J. Res. Develop. 6, 58 (1962).

[16]R. Kagiwada, M. Levy, I. Rudnick, H. Kagiwada, and K. Maki, Phys. Rev. Letters 18, 74 (1967).

[17]B. T. C. van der Hoeven and P. H. Keesom, Phys. Rev. 134, A1320 (1964).

[18]A brief reference to these data was made in the discussion (B7.2) of W. F. Vinen, C. E. Gough, E. M. Forgan, and M. J. Hood, in *Proceedings of the Eleventh International Conference on Low Temperature Physics*, 1968, edited by J. F. Allen *et al.* (University of St. Andrews Printing Department, St. Andrews, Scotland, 1969), p. 938.

[19]The paremeters given in Ref. 16 for the RRR-150 niobium sample are deduced from an one-band consideration of the niobium sample and so are not applicable to a two-band analysis of the superconducting properties; C. C. Sung, Phys. Rev. 187, 548 (1969).

[20]P. G. de Gennes, Physik Kondensierten Materie 3, 70 (1964).

[21]W. Pesch, Phys. Letters 28A, 71 (1968).

[22]I. Peschel, Solid State Commun. 4, 495 (1966).

[23]The evaluation of the density-density correlation functions follows the procedure used in H. A. Cerdeira, W. N. Cottingham, and A. Houghton, Solid State Commun. 7, 1409 (1969).

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Temperature Dependence of the Weak Ferromagnetic Moment of Hematite

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A recent proposal by Searle and Dean, which ascribes the anomalous temperature dependence of the weak ferromagnetic moment of hematite to a *large temperature-dependent* inclination of the antiferromagnetic axis out of the basal plane above the Morin temperature, is demonstrated to be incompatible with Mössbauer data. Some possible explanations of this effect are noted.

Recently Searle and Dean[1] have measured the temperature dependence of the weak ferromagnetic moment m of hematite (α-Fe_2O_3) above its Morin transition[2] ($T_M \simeq 260\,^\circ$K), and, in agreement with a prior study by Flanders and Schule,[3] they found that m drops more slowly than the sublattice magnetization M. The observed increase of m/M is rather unexpected. The usual molecular-field treatment of the

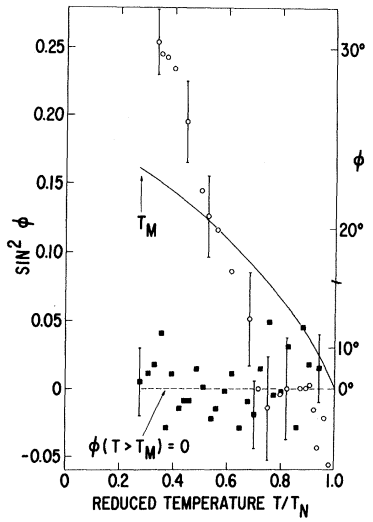

FIG. 1. Temperature dependence of the angle ϕ between the antiferromagnetic axis of hematite and the basal plane, for $T > T_M$. The solid squares give the value of ϕ determined from Van der Woude's (Ref. 9) measurements of the quadrupole splitting, using powdered material. The error bars include the uncertainty in the value of the quadrupole splitting for $T \ll T_M$. The open circles give the value of ϕ determined using the data and normalization of Searle and Dean (Ref. 1) for m/M, and assuming the validity of Eq. (2). The full line corresponds to Searle and Dean's calculation of $\phi(T)$ from (2) and the anisotropy energy [see Eq. (6) ff. and Fig. 2 of Ref. 1].

two-sublattice approximation[4,5] to the Hamiltonian

$$\mathcal{H} = J\,\vec{S}_1 \cdot \vec{S}_2 + \vec{D} \cdot \vec{S}_1 \times \vec{S}_2 \qquad (1)$$

for hematite predicts m/M to be constant with temperature, and this is borne out[6] in other weak ferromagnets.

Searle and Dean[1] attribute the variation in m/M to a *predicted large temperature-dependent* tilt ($20° - 30°$ at room temperature) of the antiferromagnetic axis of hematite out of the basal (111) plane. They find

$$m/M \propto \cos\phi(T), \qquad (2)$$

where $\phi(T)$ denotes the angle between the antiferromagnetic axis $\vec{l} = \vec{S}_1 - \vec{S}_2$ and the basal plane. The purpose of this note is to demonstrate that Mössbauer-effect data rule out such *large temperature-dependent* values of ϕ above T_M. We also list a few possible alternative origins for such an effect.

In hematite information, as to the mean spin direction, may be obtained both from measurements of the Mössbauer quadrupole splitting of powder spectra, and from line-intensity data using single-crystal absorbers.

a. Quadrupole splitting. It is well established[5,7] that below the Morin temperature T_M the antiferromagnetic axis in hematite lies along the trigonal [111] axis of its corundum-type structure (i.e., $\phi = \frac{1}{2}\pi$). Using the standard formula[8] for the Mössbauer quadrupole splitting Δ, we have for $T > T_M$

$$\Delta(T)/\Delta_0 = \tfrac{1}{2}[3\sin^2\phi(T) - 1]. \qquad (3)$$

In (3), Δ_0 is the quadrupole splitting for $T < T_M$.

Experimental data for $\Delta(T)$ are given by Van der Woude,[9] and we have used his results[10] to determine $\phi(T)$ for $T > T_M$ (Fig. 1). We have also plotted $\phi(T)$ using the experimental results for m/M and the normalization of Searle and Dean,[1] and assuming Eq. (2) to be valid. The full line corresponds to their[1] attempt to derive $\phi(T)$ from (2) and the temperature dependence of the anisotropy energy. They predict $\sin^2\phi(T_M) = 0.16$. [See Fig. 2 and Eq. (6) ff. of Ref. 1.]

The interpretation of Searle and Dean[1] is clearly incompatible with the Mössbauer results, which indicate a much smaller *temperature-independent* value for $\phi(T)$ above the Morin temperature. The Mössbauer measurements are, in fact, not inconsistent with the conventional view that the antiferromagnetic axis of hematite lies in the basal plane for $T > T_M$, i.e., $\phi(T > T_M) = 0$, but we cannot rule out a possible *small* ($\lesssim 10°$) nonzero value for ϕ.

b. Line intensity. In Fig. 2 we present a room-temperature Mössbauer spectrum[11] of an oriented (mosaic) crystal absorber, cut perpendicular to the [111] direction. The γ rays propagated parallel to the [111] axis. For a *thin* absorber, the line-intensity ratio (see Fig. 2 for the labeling) in such an arrangement is[8]

$$\frac{I_1}{I_2} = \frac{I_6}{I_5} = \frac{3(1+\sin^2\phi)}{4\cos^2\phi}\,. \qquad (4)$$

If $\phi = 0$ at room temperature, then (4) reduces to

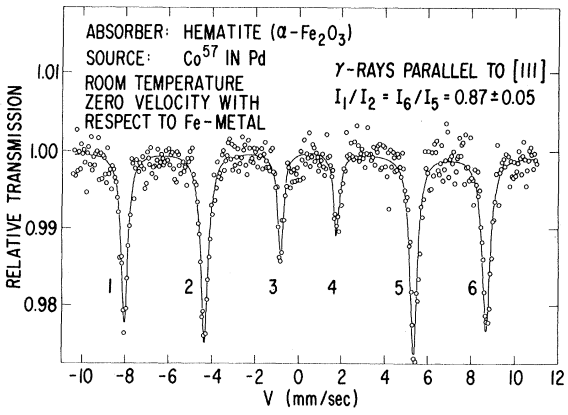

FIG. 2. Room-temperature spectrum of a crystal (mosaic) absorber of hematite (Ref. 11). The γ-ray direction was parallel to the [111] axis. The line-intensity ratio's I_1/I_2 and I_6/I_5 are given. The absorber was not "thin" and saturation broadening is evident.

$$I_1/I_2 = I_6/I_5 = 0.75. \quad (5)$$

Using the interpretation of Searle and Dean[1] and their value of m/M, we have,[12] however,

$$I_1/I_2 = I_6/I_5 \simeq 1.25. \quad (6)$$

The crystal absorber used to obtain the spectrum of Fig. 2 was unfortunately not "*thin*," and this has the effect of tending to equalize otherwise unequal peak intensities. There is, however, a clear-cut qualitative difference between (5) and (6), since if $\phi = 0$, we have $I_1/I_2 = I_6/I_5 < 1$, whereas, if the interpretation of Searle and Dean is valid, we would find $I_1/I_2 = I_6/I_5 > 1$. This distinction remains valid even for thick absorbers, and reference to Fig. 2 clearly indicates that $I_1/I_2 = I_6/I_5 < 1$, with values tending to that given in (5). Similar results were obtained on repeating the measurement.

Since our results indicate that the temperature dependence of m/M does not derive from the inclination of the antiferromagnetic axis with respect to the basal plane, we will briefly list a few possible alternative explanations of this effect.

We take the antiferromagnetic axis to lie in the basal plane. Then the molecular-field solution of (1) proceeds by minimizing

$$\langle \mathcal{H} \rangle \simeq J \langle \vec{S}_1 \rangle \cdot \langle \vec{S}_2 \rangle + \vec{D} \cdot \langle \vec{S}_1 \rangle \times \langle \vec{S}_2 \rangle , \quad (7)$$

where $\langle \cdots \rangle$ denotes the thermal average, and it follows easily[5] that the weak ferromagnetic moment m is given by

$$m/M = D/J . \quad (8)$$

The equality in (7) is not exact since we have assumed that S_1 and S_2 are not correlated. Moreover, it is by no means clear that the neglect of spin-spin correlations in the isotropic and antisymmetric exchange terms [first and second terms of (7)] introduce equivalent errors. It is thus conceivable that the actual temperature dependence of m/M is hidden by the molecular-field approximation, and an improved technique for the evaluation of $\langle \mathcal{H} \rangle$ would bring this to the fore.

A second (trivial) mechanism for the temperature variation of m/M arises if D/J is explicitly temperture dependent. It is perhaps plausible to expect D to be sensitive to lattice parameter variations, and thus thermal expansion could drive the change in m/M. Measurements of the pressure dependence of m/M (if any) would be helpful in establishing such behavior.

We must also consider the effect of higher-order invariants in the two-sublattice approximation to the Hamiltonian of hematite. A list of such terms has been given by Dzialoshinskii.[4] Clearly, terms of the form $(S_{1z}^2 + S_{2z}^2)\,(\vec{D} \cdot \vec{S}_1 \times \vec{S}_2)$, $(\vec{D} \cdot \vec{S}_1 \times \vec{S}_2)^2$, or $(\vec{S}_1 \cdot \vec{S}_2)\,(\vec{D} \cdot \vec{S}_1 \times \vec{S}_2)$ are allowed by symmetry, and will lead to a temperature dependence in m/M even in the molecular-field approximation. The magnitude of such terms might be too small to explain the observed variation however.

Finally, it should be noted that hematite is actually a four-sublattice weak ferromagnet,[1,4,5] and it is possible that a four-sublattice analysis, taking into account next-nearest-neighbor and possibly more distant spin-spin interactions, might be necessary to explain the anomalous temperature dependence of m/M.

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[1] C. W. Searle and G. W. Dean, Phys. Rev. B1, 4337 (1970).

[2] F. J. Morin, Phys. Rev. 78, 819 (1950).

[3] P. J. Flanders and W. J. Schule, *Proceedings of the International Conference on Magnetism, Nottingham*, 1964 (The Institute of Physics and the Physical Society, London, 1965), p. 594.

[4] I. E. Dzialoshinskii, Zh. Eksperim. i Teor. Fiz. 32, 1547 (1957) [Sov. Phys. JEPT 5, 1259 (1957)].

[5] T. Moriya, in *Magnetism* (Academic, New York, 1963), Vol. 1, p. 86.

[6] D. Treves, J. Appl. Phys. 36, 1033 (1965).

[7] J. O. Artman, J. C. Murphy, and S. Foner, Phys. Rev. 138, A912 (1965).

[8] G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic, New York, 1964).

[9] F. Van der Woude, Phys. Status Solidi 17, 417 (1966).

[10] Van der Woude in Ref. 9 quotes a value of $\Delta_0 = 9.63 \times 10^{-9}$ eV obtained by averaging spectra in the temperature region 162–220 °K. Since sample impurities and imperfections can lower T_M [P. J. Flanders and J. P. Remeika, Phil. Mag. 11, 1271 (1965)] by tens of degrees, we have felt it is better to determine Δ_0 as the average of spectra for $T \lesssim 170$ °K. We find $\Delta_0 = (9.95 \pm 0.3) \times 10^{-9}$ eV and have used this value in evaluating $\phi(T)$ from the quadrupole splitting in Fig. 1. Use of Van der Woude's value of Δ_0 decreases $\sin^2\phi$.

[11] Taken at the Department of Electronics, Weizmann Institute of Science, Rehovot, Israel.

[12] If we use the full line of Fig. 1 [model calculation of Searle and Dean (Ref. 1)] to estimate I_1/I_2 and I_6/I_5 at room temperature, we find, similarly, $I_1/I_2 = I_6/I_5 = 1.03 > 1$.