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Comments

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On the interpretation of muon-spin-rotation experiments in orthoferrites

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Results of the recently reported muon-spin-rotation (μSR) study on the rare-earth orthoferrites (RFeO$_3$) are discussed. An outline for a more complete interpretation of the μSR results of RFeO$_3$, based on muon bonding and motion and covalency, is presented. Muon behavior appears to be similar in various magnetic oxide structures.

Recently Holzschuh *et al.*[1] reported muon-spin-rotation (μSR) investigations of the rare-earth orthoferrites (RFeO$_3$). Basically it was found that in RFeO$_3$ the muon localizes near an oxygen and engages in a muon-oxygen bond. Their results, supported by excellent dipole calculations are in reasonable agreement with the interpretation of the μSR data on the antiferromagnetic corundum-structured oxides[2,3] like hematite (α-Fe$_2$O$_3$). In both studies the origin of the local magnetic field at the muon site is of great importance in order to understand muon behavior. Its source may come from local magnetic dipoles or unpaired spin density arising from covalency effects (supertransfer hyperfine field contributions). Muon motion at elevated temperatures plays a role in averaging these local fields.

μSR results, obtained for α-Fe$_2$O$_3$, provided for the first time[3] and in a most direct way evidence that muon-oxygen bonding can occur in oxides, and that long-lived metastable muon states[4] may be present in magnetic oxides well below room temperature. The μSR-orthoferrite results and the interpretation as brought forward by Holzschuh *et al.* are consistent with these earlier findings; however, their interpretation contains some serious flaws: important details have not been worked out correctly and their analysis is not complete enough to support some of their conclusions. In this Comment we would like to address these omissions and outline directions to obtain a better interpretation of the μSR results in the orthoferrites.

In their presentation it is claimed that the muon hyperfine field at the muon site in the orthoferrites can be explained in terms of dipolar fields (B_{dip}) *only*. Although thermal lattice expansion is used to try to explain a minor, but important (see later), detail (a small deviation from the magnetization curve, see Sec. III D of Ref. 1), they fail to report the B_{dip} variation as a function of the lattice parameter in the orthoferrite series.

It is reasonable to assume that the muon stopping site for the most stable state located in site (2) (Ref. 1), which we shall call henceforth the Holzschuh site, is the same for all the orthoferrites. The Holzschuh site can be described as to be near the center of a slightly distorted square of the nearest rare-earth ions (see Fig. 10, Ref. 1). It can be easily shown that these B_{dip} variations are of the order of 5% while the muon hyperfine field (extrapolated to 0 K) varies 300% for the measured set of orthoferrites. In Fig. 1 and

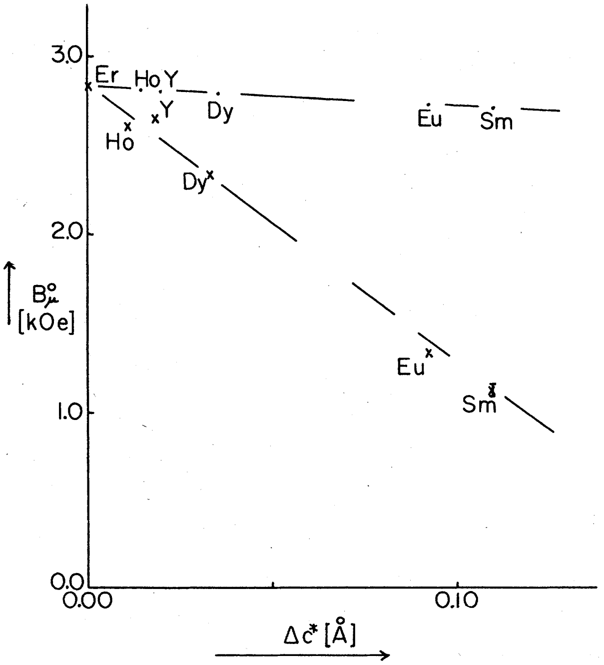

FIG. 1. Actual (×) and predicted (·) (based on results of Ref. 1) muon hyperfine field behavior as a function of $\Delta c^*(=c_R^*-c_{\text{Er}}^*)$. c^* is an average measure of the lattice parameter, defined in the Table I caption. As can be seen the predicted trend (based upon *pure* dipole calculations) of the measured internal field, when going through the orthoferrite series is not correct.

Table I we show the predicted B_μ behavior (based on the B_{dip} only interpretation) and the comparison with the actual behavior. As a calibration point we have chosen the Holzschuh site found for $\mathrm{ErFeO_3}$ (see Table II, Ref. 1); very similar results can be obtained if the other sites as reported for $\mathrm{YFeO_3}$ or $\mathrm{SmFeO_3}$ are taken as reference.

It must be noted that B_{dip} varies strongly with position (about 10 kOe/Å) near these sites. This fact makes it possible to find B_{dip} values for sites very near each other fitting the measured muon fields in $\mathrm{ErFeO_3}$, $\mathrm{YFeO_3}$, and $\mathrm{SmFeO_3}$ as reported by Holzschuh *et al.* However, this also causes their error in the muon-oxygen distance to be of the order of 0.1 Å.

We would like to stress that for muon states in $R\mathrm{FeO_3}$ the μ–O distance has to be taken to be 1 Å if one assumes a μ–O bond. Potential-energy considerations[2,5] strongly support this characteristic bondlength. Taking this feature explicitly into account, the obvious discrepancy shown in Fig. 1 indicates that pure dipolar fields cannot explain the observed behavior.

μSR studies[2] in antiferromagnetic oxides have shown that in addition to B_{dip} a supertransfer hyperfine field contribution (B_{sthf}) must be considered. As reported by Holzschuh *et al.*,[1,6] two extreme assumptions ($B_{\mathrm{dip}}=0$ or $B_{\mathrm{sthf}}=0$) regarding the muon hyperfine field resulted in nearly the same possible stopping sites, one of which is the Holzschuh site. Relying heavily upon theoretical results,[7] concerning the magnetic ordering and relative orientation of the iron spins, it was concluded that a hyperfine field contribution could be neglected.

This result was substantiated by the field-induced spin canting effect in $\mathrm{YFeO_3}$, which strongly indicates that the major part of the muon hyperfine field is of dipolar origin.[1] Another experimental argument for a major dipolar field contribution is that only very slight deviations from a trend following the magnetization curve for the μSR frequency signals are observed. Owing to covalency effects strong deviations occur for α-$\mathrm{Fe_2O_3}$.[2]

Simple theoretical considerations, similar to arguments used in a covalency model for the antiferromagnetic oxides show that for the Holzschuh site B_{sthf} can be estimated to be zero to first order.[2] As discussed above, however, a pure dipole field cannot explain the muon hyperfine field data in $R\mathrm{FeO_3}$; thus, second-order covalency effects need to be considered.

TABLE I. Lattice parameters and a comparison of measured and predicted (based on results of Ref. 1) muon hyperfine fields.

R	c^* (Å)	B_{dip} (kOe)	θ_1 (deg)	$\cos^2\theta_1$ · · ·	$B_\mu^0(0)$ (kOe)
Sm	7.755	2.74	148.9	0.733	1.15
Eu	7.738	2.76	147.8	0.716	1.31
Dy	7.681	2.80	145.0	0.671	2.32
Y	7.665	2.81	143.6	0.648	2.66
Ho	7.660	2.81	144.1	0.656	2.57
Er	7.645	2.83	142.7	0.633	2.83
Footnote	a	b	c		d

[a] $c^*=[2(a^2+b^2)^{1/2}+c]/3$, where a, b, and c are the lattice constants (taken from Refs. 8 and 9).

[b] The predicted B_{dip} values, assuming the Holzschuh site, reported for $\mathrm{ErFeO_3}$ (Table II, Ref. 1), is assumed to be the same for all the orthoferrites. The muon oxygen distance is taken to be 1 Å.

[c] Measured values for the Fe–O–Fe bond angle (θ_1) along the c direction (Refs. 8 and 9).

[d] Extrapolated values of the local muon field at 0 K. The errors are of the order of 1% or less, except for Sm, where the absolute error is 0.04.

That covalency effects are present can be best seen in Fig. 2 (see also Table I) where the μSR frequencies, scaled to 0 K, for the configuration is plotted as a function of $\cos^2\theta_1$, where θ_1 is the measured Fe–O–Fe bond angle[8,9] along the c direction, which is the required angle for the Holzschuh site. An excellent linear dependence can be seen. We note that this dependence is in the opposite direction as observed for the hyperfine field at the Fe site and for the Neél temperature in the orthoferrite series.[10] Thus, supertransfer fields for the idealized orthoferrite ($\theta=\pi$ rad) are maximal at the iron sites and minimal (zero) at the muon site. We have begun dipolar calculations for this orthoferrite to search for all (meta)stable stopping sites using extrapolated field values to $\theta=\pi$ rad and to 0 K.

Independently, as has been done for α-$\mathrm{Fe_2O_3}$,[2] we have also started to perform the necessary potential-energy calculations considering muon-oxygen bond formation. Electrostatic and structural arguments suggest more possible sites in the perovskite structure than the reported Holzschuh site. These considerations do not support the suggestion made by Holzschuh *et al.* that the "other" sites are not far away from the rare-earth–oxygen plane.[1] In the perovskite structure, there are two structurally inequivalent oxygen sites, available for muons participating in a muon-oxygen bond. At least three probable stopping sites may be found: one in the rare-earth–oxygen plane (Holzschuh site), one in the iron-oxygen plane, and sites located between oxygen planes.

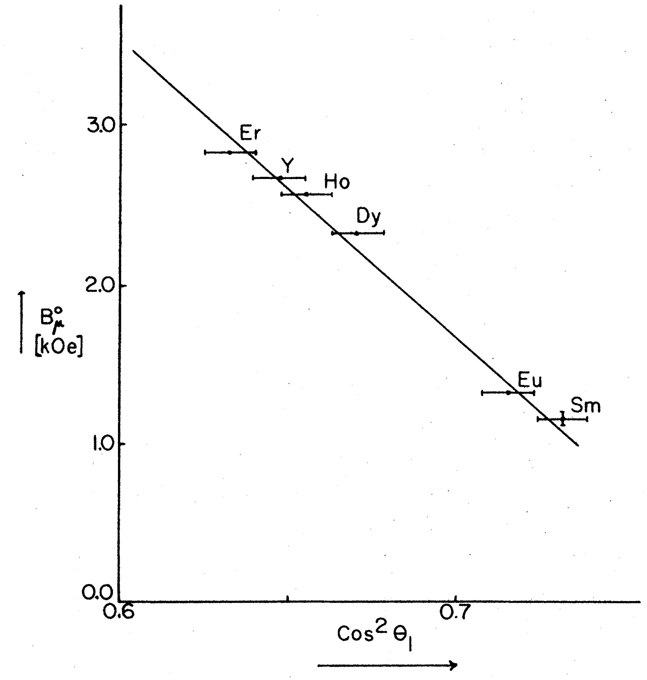

FIG. 2. Extrapolated muon hyperfine field $[B_\mu^0(0\ \mathrm{K})]$ as a function of $\cos^2\theta_1$. θ_1 is the Fe–O–Fe bond angle along the c direction. Note the reversed order for Y and Ho with respect to Δc^* (compare with Fig. 1).

In their paper[1] it is also brought forward that the high muon relaxation rate at high temperature can be explained by a crystal defect model. The presence of impurities and other defects can influence the muon behavior, but here, owing to the overall presence of the oxygen ions, the muon-oxygen bonding process is expected to play an overwhelming role.

If one compares the muon relaxation rates as a function of temperature for magnetically and structurally different oxides (α-Fe_2O_3, Fe_3O_4, $ErFeO_3$, and $YFeO_3$)[1,2,11] for which no magnetic transitions occur between room temperature and 600 K it can be seen (see Fig. 3) that the λ increase starts above 360 K. These data suggest that the muon is behaving similarly in various magnetic oxides, indicating that impurity effects are not dominant.

A consistent explanation is that the muons are localized in muon-oxygen bonding states well below room temperature; going up in temperature, local diffusion sets in; above 500 K global diffusion through the whole lattice takes place. The deviation of the μSR frequency from the magnetization curve for $YFeO_3$ at 450 K (see Sec. III D, Ref. 1) may then be due to the transition from local to global muon diffusion, which changes the manner in which the muon samples the magnetic environment.

In their discussion muon relaxation processes for $SmFeO_3$ and α-Fe_2O_3 are compared and found similar. In both cases the hopping muon sees hyperfine fields of opposite directions and thus the relaxation rate (λ) increases with temperature. However, for α-Fe_2O_3 this strong λ increase starts above 400 K, while for $SmFeO_3$ it begins around 300 K. This difference may then be due to the combined effect of the transition from local to global muon diffusion and the occurrence of the Γ_2 (instead of Γ_4) spin configuration below 480 K.

The activation energies of this thermally activated global diffusion process are on the order of 400 meV, which is determined from the temperature-dependent relaxation data. The activation energies of the local diffusion process occurring well below room temperature are of the order of 100 meV. Such energies are characteristic for hydrogen (muon)-oxygen bonding.[5]

In conclusion, basic concepts in the interpretation of the muon hyperfine interactions in the rare-earth orthoferrites are muon-oxygen bonding, muon motion, and covalency. The latter is responsible for a supertransfer hyperfine field contribution, which must not be disregarded. Potential-energy calculations are needed to complete the hyperfine field search calculations for the explanation of the μSR-orthoferrite results.

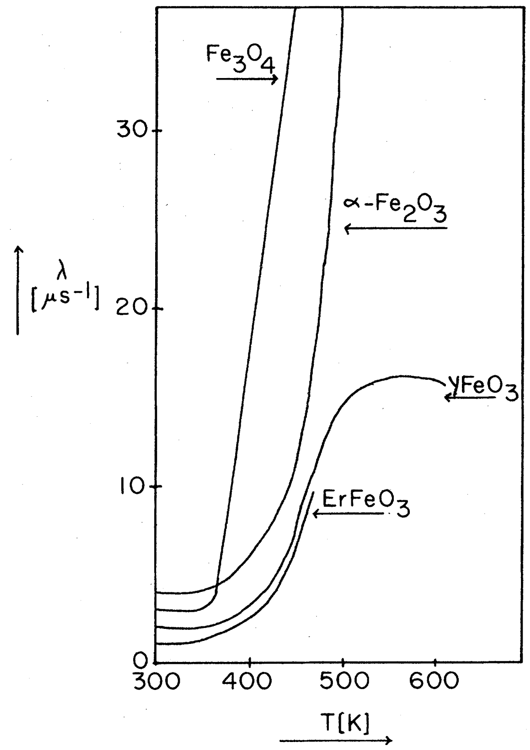

FIG. 3. Temperature dependence of the relaxation rate in the temperature region (300,600 K) of the magnetic oxides Fe_3O_4, α-Fe_2O_3, $YFeO_3$, and $ErFeO_3$. For comparison purposes the data have been smoothed. The flattening of the $\lambda(T)$ curve above 500 K for the orthoferrites is due to the decreasing magnetization (Ref. 1). The Neél temperatures of the orthoferrites are about 650 K.

We wish to thank W. P. Hofmann for his fruitful and indispensable participation in "building muoxyl bridges," especially in the early days of muon-spin rotation in magnetic oxides. Stimulating discussions with A. B. Denison who suggested the $\cos^2\theta$ dependence and A. M. Stoneham are gratefully acknowledged.

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[1] E. Holzschuh, A. B. Denison, W. Kündig, P. F. Meier, and B. D. Patterson, Phys. Rev. B **27**, 5294 (1983).

[2] C. Boekema, in *Proceedings of the Yamada-μSR 83-Conference, Shimoda, Japan* [Hyper. Inter. **17–19**, 305 (1984)]; C. Boekema, A. B. Denison, and K. J. Rüegg, J. Magn. Magn. Mater. **36**, 111 (1983); K. J. Rüegg, thesis, Physik Institut, University of Zürich, Switzerland, 1981; C. Boekema, K. J. Rüegg, and W. P. Hofmann, Hyper. Inter. **8**, 609 (1981); K. J. Rüegg, C. Boekema, W. Kündig, P. F. Meier, and B. D. Patterson, *ibid.* **8**, 547 (1981).

[3] K. J. Rüegg, C. Boekema, A. B. Denison, W. P. Hofmann, and W. Kündig, J. Magn. Magn. Mater. **15–18**, 669 (1980).

[4] A. M. Browne and A. M. Stoneham, J. Phys. C **15**, 2709 (1982).

[5] M. D. Joesten and L. J. Schaad, *Hydrogen Bonding* (Dekker, New York, 1974).

[6] E. Holzschuh, C. Boekema, W. Kündig, K. J. Rüegg, and B. D. Patterson, Hyper. Inter. **8**, 615 (1981).

[7] The sign convention, labeling of the iron ions and the representation of the spin configurations is not uniform in the literature [D. Treves, Phys. Rev. **125**, 1843 (1962)]; E. F. Bertaut, in *Magnetism III*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963); G. F. Hermann, Phys. Rev. **133**, A1334 (1964); R. L. White, J. Appl. Phys. **40**, 1061 (1969); H. Lutgemeier *et al.*, J. Magn. Magn. Mater. **21**, 289 (1980). For example, if we follow White, Fig. 2 in Ref. 1 does not reflect the spin rotation in $ErFeO_3$. This all casts doubt in using theoretical relations, concerning the iron spin configurations and their orientation.

[8] P. Coppens and M. Eibschutz, Acta Crystallogr. **19**, 524 (1965).

[9] M. Marezio, J. P. Remeika, and P. D. Dernier, Acta Crystallogr. **B26**, 2008 (1970).

[10] G. A. Sawatzky and F. van der Woude, J. Phys. (Paris) Colloq. **12**, C6-47 (1974).

[11] C. Boekema, V. A. M. Brabers, A. B. Denison, R. H. Heffner, R. L. Hutson, M. Leon, C. E. Olsen, and M. E. Schillaci, J. Magn. Magn. Mater. **31–34**, 709 (1983).