MAGNETIC ORDER IN CERTAIN ALKALI AMPHIBOLESA MÖSSBAUER INVESTIGATION

R. Borg, I. Borg

HAL Id: jpa-00215730
https://hal.science/jpa-00215730

MAGNETIC ORDER IN CERTAIN ALKALI AMPHIBOLES
A MÖSSBAUER INVESTIGATION

R. J. BORG and I. Y. BORG

Lawrence Livermore Laboratory, University of California
Livermore, California 94550, USA

Résumé. — L'apparition d'éclatement magnétique hyperfin (mhfs) a été utilisée pour déterminer la température de transition magnétique dans quelques amphiboles alcalines. Cette classe de minéraux a une structure cristallographique monoclinique et une formule générale

$$(Na, Ca)_{2-3}(Fe^{+2}, Fe^{+3}, Mg, Al)_5Si_8O_{22}(OH, F)_2 .$$
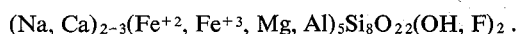
Le fer peut occuper trois sites cristallographiques distincts, cependant l'éclatement magnétique hyperfin disparaît lorsque la température augmente tout comme dans des substances magnétiques moins complexes.

Malgré la complexité globale, la valeur beaucoup plus élevée de mhfs pour Fe^{3+} sépare aisément les lignes 1 et 6 de l'ensemble de l'absorption résonnante due à Fe^{2+}. En conséquence, des paramètres Mössbauer et magnétiques significatifs peuvent être déterminés. La variation de mhfs avec la température s'écarte nettement de la fonction de Brillouin habituelle.

Des données de susceptibilité magnétique sur l'un des échantillons révèlent la nature antiferromagnétique de l'ordre. La séquence d'empilement des trois sites forme une chaîne unidimensionnelle parallèle à l'axe c. Chaque chaîne est séparée de la chaîne adjacente par des tétraèdres SiO_4 pontés. Ainsi l'échange direct ne peut avoir lieu qu'à l'intérieur de la chaîne et une sorte de super-échange doit exister entre les chaînes.

Abstract. — The appearance of magnetic hyperfine splitting (mhfs) has been used to determine the magnetic ordering temperature for a few selected alkali amphiboles. This class of minerals has the monoclinic crystal structure and the general formula

$$(Na, Ca)_{2-3}(Fe^{+2}, Fe^{+3}, Mg, Al)_5Si_8O_{22}(OH, F)_2 .$$
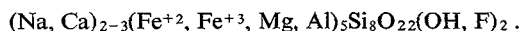
The iron can occupy three distinct crystallographic sites, yet the mhfs collapses with increasing temperature in the manner of less complex magnetic substances.

In spite of the overall complexity, the much greater mhfs of Fe^{+3} easily separates lines 1 and 6 from all resonant absorption due to Fe^{+2}. Thus, relevant Mössbauer and magnetic parameters can be determined. The temperature dependence of the mhfs departs substantially from the usual Brillouin-like function.

Magnetic susceptibility data on a single specimen indicates the ordering to be antiferromagnetic. The stacking sequence formed by the three sites is a one-dimensional chain parallel to the c axis. Each chain is separated from adjacent chains by linked SiO_4 tetrahedra. Thus, direct exchange can only occur within the chain, and a type of super-exchange must exist between chains.

1. **Introduction.** — Alkali amphiboles have the general formula

$$(Na, Ca)_{2-3}(Fe^{+2}, Fe^{+3}, Mg, Al)_5Si_8O_{22}(OH, F)_2$$
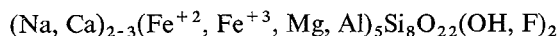
and belong to the monoclinic crystal system. We have selected several compositions from the iron-rich members of the mineral group to be used as absorbers for Mössbauer spectroscopy. Spectra have been obtained from cryogenic to room temperatures with absorbers consisting of randomly oriented powders, as well as oriented single crystals. In our preliminary investigation three of the four minerals demonstrate magnetic ordering at 2.67 K or above, and it would appear that all would order if our cryostat were capable of achieving lower temperatures. While magnetic ordering has been observed in other silicates, such as Fe_2SiO_4 [1],

$$(Fe, Mg) SiO_3 \text{ [2] and } Al_2Fe_3(SiO_4)_3 \text{ [3] },$$
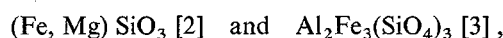
amphiboles are structurally the most complex silicates for which magnetic hyperfine spectra have been recorded. We have previously reported [4] on the extremely high accuracy of Fe^{+2}/Fe^{+3} ratios calculated from magnetic hyperfine spectra of Fe^{+3}, in which lines 1 and 6 are clearly separated from Fe^{+2} lines. In this report we shall comment briefly on the purely magnetic aspects of these experiments which are still in progress.
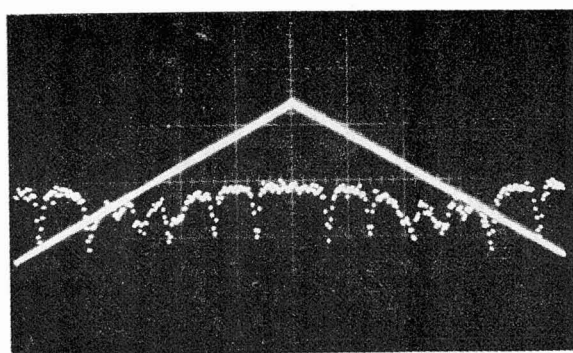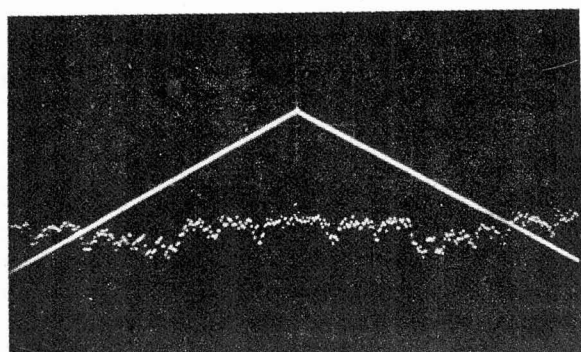
SP-1 at 4.6°K
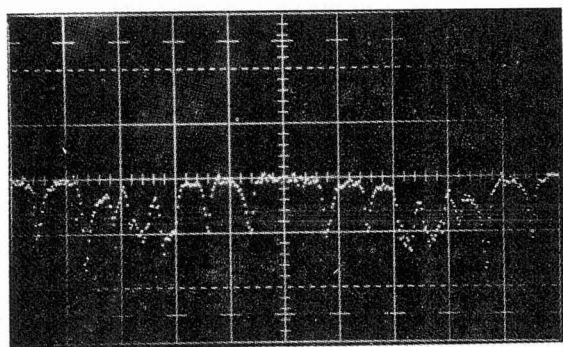
RDR-1 at 4.6°K
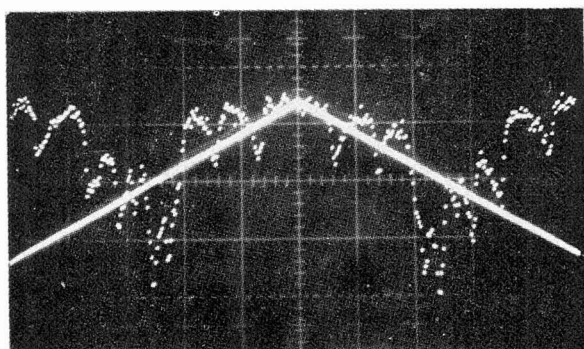
331-M-56 at 4.6°K

331-M-56 at 2.7°K

FIG. 1. — The magnetic hyperfine spectra of the alkali amphiboles 331-M-56, RDR-1 and SP-1.

2. Fe-rich cation chains. — The magnetically ordered amphiboles offer an excellent material in which to study magnetic order of one-demensional magnetic chains. The Fe ions occupy three distinct octahedrally coordinated crystallographic sites [5]. By convention they are labeled M_1, M_2 and M_3. They are aligned parallel to the c crystallographic axis in the following stacking sequence : (2 3 2) (1 1) (2 3 2) (1 1)... The Fe^{+2} ion predominantly occupies sites 1 and 3, leaving site 2 for occupation by Fe^{+3}. Each chain is made up of the above sequence of nearest-neighbor Fe sites, but is itself separated from nearest-neighbor chains by linked SiO_4 tetrahedra, so that direct exchange occurs only within the chain, and some form of super-exchange must prevail between chains. As yet the magnetic structure is unknown, and a description of the experimental results to date must suffice.

3. Experimental. — The Mössbauer spectrometer, of the constant acceleration variety, is used in conjunction with a proportional counter and a 400-channel (velocity) storage bank. The specimen temperature is measured with a calibrated carbon resistance thermometer. A Zener diode is used as an internal heater to maintain temperatures above 4.6 K. Pumping on the liquid helium reservoir has produced temperatures as low as $\sim$ 2.6 K. Sources were $\sim$ 25-35 mCi of ^{57}Co in Cu, and $\sim 10^6$ counts/channel were allowed to accumulate. Velocities are relative to iron.

4. Results. — Figure 1 shows the magnetic hyperfine split spectra of three amphiboles, designated 331-M-56, RDR-1 and SP-1 (see ref. [4] for chemical analyses). The relevant Mössbauer and magnetic parameters are given in Table I, where T_0 designates

TABLE I

Mössbauer and magnetic parameters

	T_0	q. s.	i. s.	m. h. f. s.	kG
331-M-56	6.2	0.22	− 0.848	17.55 ([a])	546
RDR-1	22.5	0.32	− 0.968	17.66	549
SP-1	26.0	0.31	− 0.993	17.53	545

([a]) Value at 2.67 K.

the commencement of magnetic order in K, q. s. the quadrupole splitting, i. s. the isomer shift, and m. h. f. s. the magnetic hyperfine splitting. All values are given in mm/s and pertain only to Fe^{+3} at 4.6 K.

Figures 2 and 3 illustrate the temperature dependence of the quadrupole and isomer shifts for both oxidation states and all crystallographic sites. These data were obtained by unfolding the paramagnetic spectra in a conventional manner using a computer code that places no constraints upon either line width or amplitude of the constituent Lorentzians. The

relatively large temperature dependence of the qua-
drupole splitting indicates that the Fe^{+2} is in a high
spin state (see Fig. 2). The high absolute values of the
essentially temperature-independent Fe^{+3} quadrupole
splitting allow one to conclude that it, too, is in the
high spin state. The plots shown in figures 2 and 3 are
only intended to show the general range and trend of
the data ; several additional determinations will be
necessary in order to determine the true functional
dependence of q. s. and i. s. upon temperature.

Preliminary magnetic measurements on SP-1 reveal
typical antiferromagnetic behavior (unpublished data,
courtesy of Professor David Sellmyer, University of
Nebraska). The similarity in both structure and che-
mical composition allows one to assume that all
compositions will order in the same manner ; however,
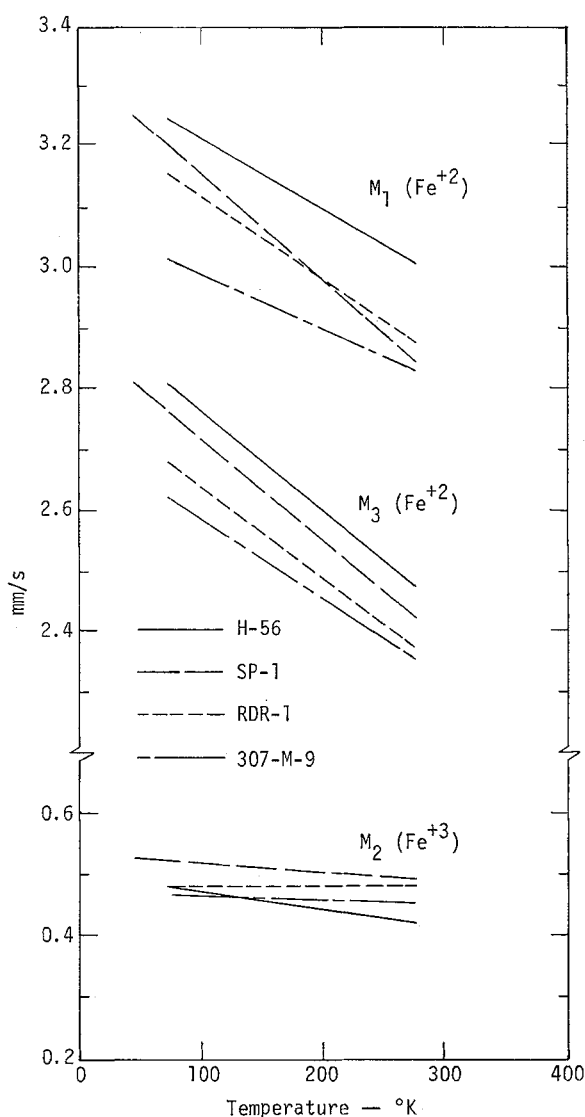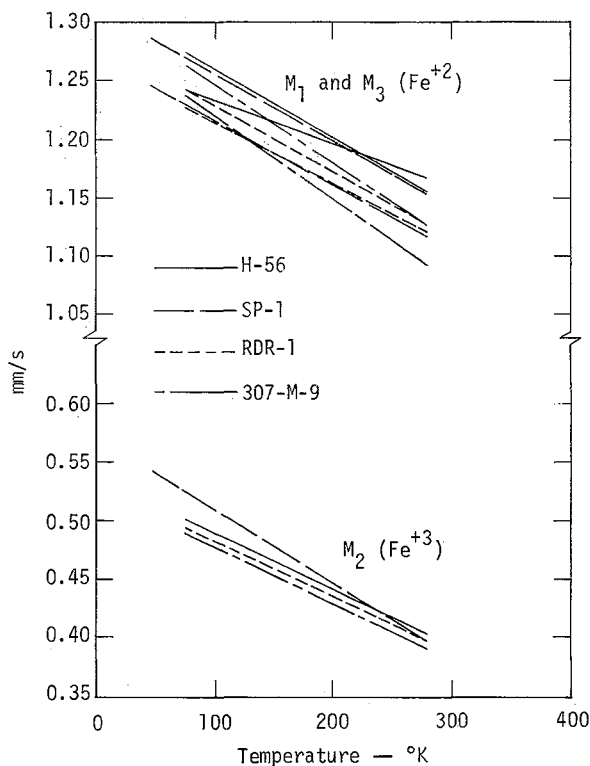this has yet to be demonstrated unequivocally.

FIG. 3. — The temperature dependence of the isomer shift in
four amphiboles. The uppermost line of the top pair corresponds
to the M_1 (Fe^{+2}) sites, and the lower to the M_3 (Fe^{+2}) site.

Figure 4 shows the temperature dependence of the
m. h. f. s. of specimen RDR-1. It is obvious that it
shows a substantial departure from the usual « Bril-
louin-like » function. Perhaps this is not surprising in
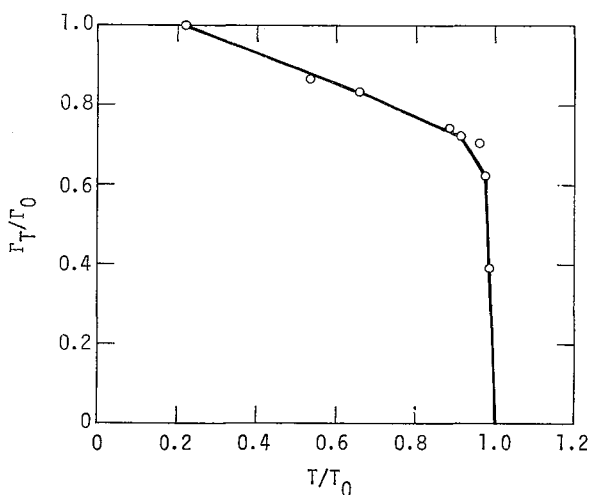view of the complexity of the structure.

FIG. 4. — The temperature dependence of the reduced magnetic
hyperfine spectra as a function of reduced temperature for
specimen RDR-1.

FIG. 2. — The temperature dependence of the quadrupole shifts
for M_1, M_2 and M_3 crystallographic sites in four alkali amphi-
boles.

Mineral SP-1 is the only one that is of sufficient size
to permit examination of oriented single crystals.
Absorbers were made of sections parallel to (100),

(110), (010) and (001). Although there are small qualitative differences in the appearance of these spectra, it has thus far proven impossible to deduce a magnetic structure for these substances. This research is continuing, however, and magnetization measure- ments on oriented single crystals are expected to provide additional insight into the solution.

References

[1] KÜNDIG, W., CAPE, J. A., LINDQUIST, R. H. and CONSTABA-RIS, G., *J. Appl. Phys.* **38** (1967) 947.

[2] SHENOY, G. K., KALVIUS, G. M. and HAFNER, S. S., *J. Appl. Phys.* **40** (1969) 1314-1316.

[3] PRANDL, W. and WAGNER, F., *Z. Kristallogr.* **134** (1971) 344-349.

[4] BORG, R. J., LAI, D. Y. F. and BORG, I. Y., *Nature Phys. Sci.* **246** (1973) 46-48.

[5] PAPIKE, J. J. and CLARK, J. R., *Am. Mineralogist* **53** (1968) 1156-1173.