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Paramagnetic Resonance of Fe^{3+} in some Feldspars

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With 4 figures and 2 tables in the text

Abstract

The EPR spectrum of Fe^{3+} in oligoclase, microcline and some other feldspars has been investigated at 35000 Mc/s and 9500 Mc/s. The parameters of the Hamiltonian spin were calculated. A comparison of the orientation of the g-factors and of the principal directions of electric field gradients leads to the assignment of Fe^{3+} to the T_1 (o) site.

INTRODUCTION

The electron paramagnetic resonance (EPR) investigation of Fe^{3+} in feldspars is related to many problems.

Firstly, it is the most direct method of obtaining complete data about the position of iron impurities in feldspars. This technique has enabled a great deal of new information concerning this old problem to be obtained (COOMBS, 1960).

Still more interesting is the use of Fe^{3+} ions as a kind of probe giving information about the interaction of the Fe^{3+} ions with their surroundings.

If the iron ions enter feldspars substitutionally for the Al^{3+} ions and if Fe^{3+} follows Al^{3+} as regards the $\text{Al} \rightleftharpoons \text{Si}$ distribution among tetrahedral sites, it would then be possible to use Fe^{3+} for investigating order-disorder relations, composition changes and twinning in members of the feldspar group.

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From the EPR point of view the complicated series of feldspar solid solutions with their order-disorder relations are highly suited for studying the further possibilities of this method. The triclinic local symmetry of Al-O_4 tetrahedra permits an investigation of the interaction of paramagnetic ions with non rhombic crystal fields.

Feldspars are compounds which like corundum, spinel, beryl (G. BURNS and W. J. NICHOLSON, 1963), spondumene (A. MANOOGIAN, F. HOLUJ, and J. W. CARSWELL, 1965) permit the comparison of crystal field by several methods: the values of eQq/h of Al^{3+} host atoms from electric quadrupole resonance spectra (ST. HAFNER and P. HARTMANN, 1964), the values of eQq/h of Fe^{57} impurity atoms from the Mössbauer techniques; and the terms in the EPR Hamiltonian spin of paramagnetic ions Fe^{3+} , Cr^{3+} , replacing Al^{3+} .

The single-crystal spectrum of the Fe^{3+} in Al-O_4 feldspar tetrahedra can be used in connection with the interpretation of tetrahedral Fe^{3+} EPR spectra in glasses (T. G. CASTNER a. o., 1960) and in powders (E. BOESMAN and D. SCHOEMAKER, 1961).

The EPR spectrum of Fe^{3+} in microcline has recently been measured by U. HÖCHLI (1964) at frequencies 8880, 9990 and 11340 Mc/s. However, the spectra at X-band frequencies (about 9500 Mc/s) are very complicated and the analysis of the spectrum in this band is extremely difficult as may be seen from Figures 1, 2 and 3 of this paper.

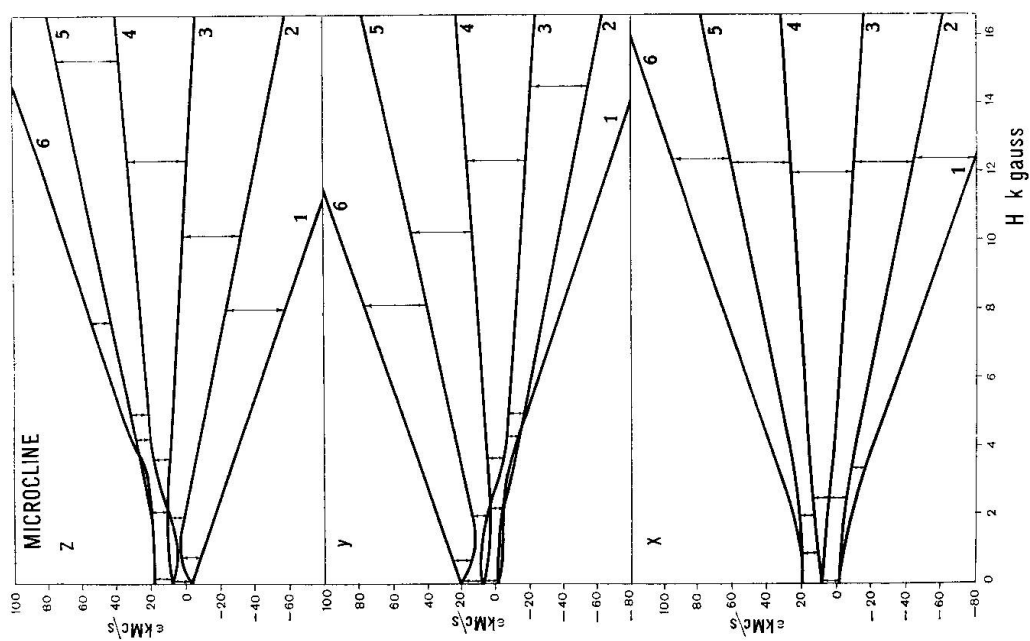
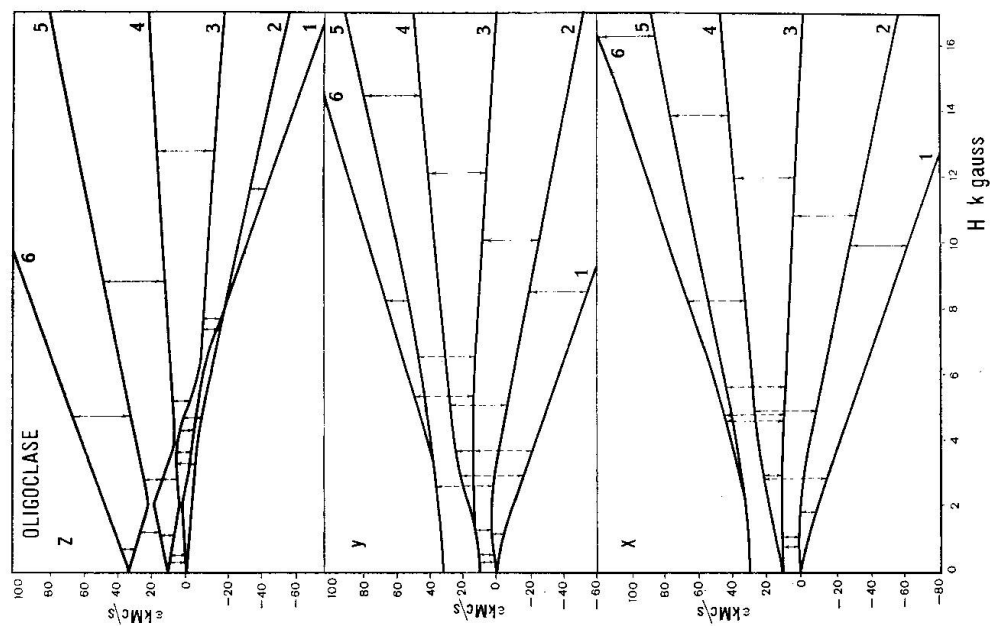
We have investigated the spectra of Fe^{3+} in oligoclase (A. S. MARFUNIN and J. MICHOUlier, 1966) and microcline at frequencies 35000 Mc/s (Q-band) and 9500 Mc/s (X-band). Preliminary results have been obtained for low sanidine and some other feldspars.

In an earlier paper the applications of EPR to mineralogy were considered (A. S. MARFUNIN, 1965).

EXPERIMENTAL PART

Measurements were made with an Q-band spectrometer (Institut Fourier, Grenoble) and an X-band spectrometer (Institute for Ore Deposits Geology, Petrology, Mineralogy and Geochemistry, Moscow).

Two different techniques were used in the determination of the principal directions of the magnetic axes: 1. by finding the extreme positions of resonance lines displayed on an oscilloscope, and 2. by plotting curves of equal magnetic field on a Fedorov sphere (B. I. ZUKERMAN, M. L. MEILMAN, L. P. SOROKINA, 1962).

Fig. 1. Energy-level diagram for Fe^{3+} in microcline.Fig. 2. Energy-level diagram for Fe^{3+} in oligoclase.

The data obtained from the measurements were treated in an "Strela" computer program.

The investigated specimens were as follows:

1. Oligoclase from pegmatites, North Karelia, Ab_{90}, An_{10} , $2V = +80^\circ$, white with blue schiller; only very thin albite twins.
2. Microcline from nepheline syenites, Khibin massiv (Kola peninsula), $2V = -82^\circ$, $\perp(010)$ $Ng = 18,5^\circ$, $\perp(001)$ $Nm = 12^\circ$. Large microcline twins. Colour white to grey.
3. Low sanidine-"Fe-orthoclase" from Madagascar, $2V = -38^\circ$ in $\perp(010)$. Colourless, semi-transparent.

The iron content is 0,0n% in oligoclase, 0,n% in microcline and 0,5—p,7% in sanidine (spectrophraphic analysis).

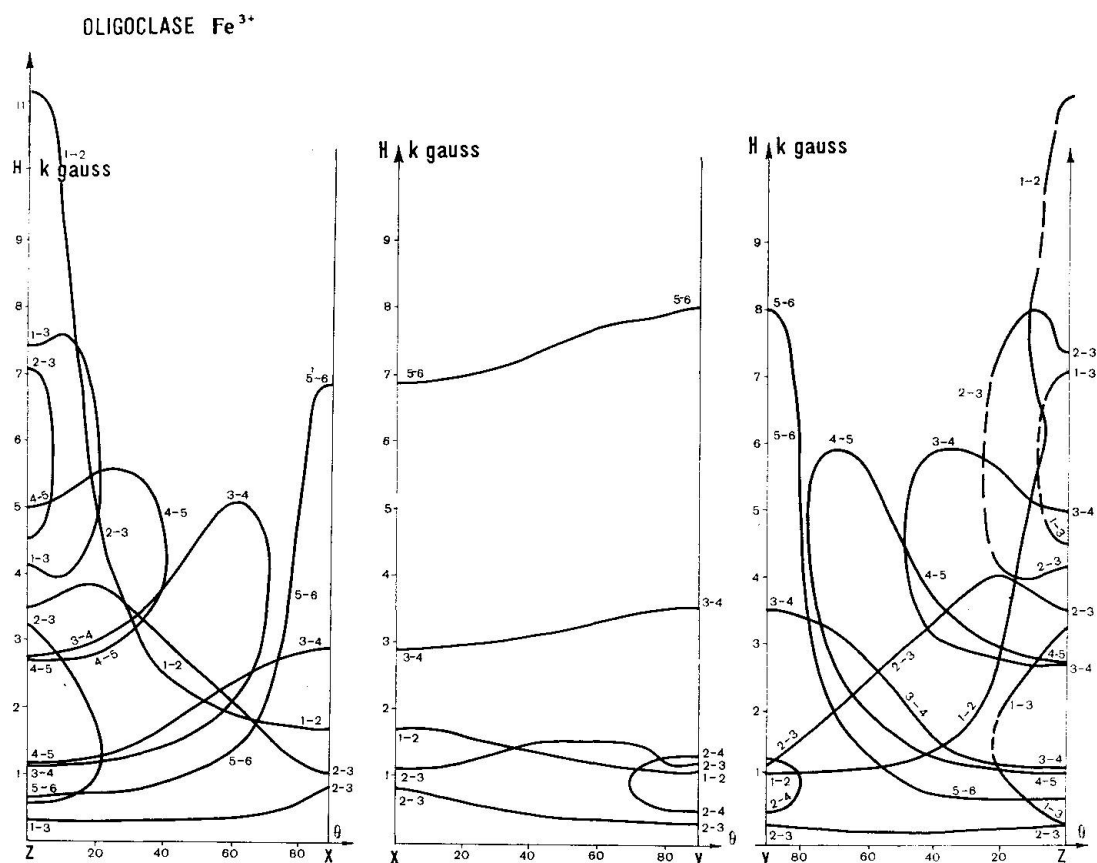


Fig. 3. Angular dependence of the EPR spectrum of Fe^{3+} in oligoclase at 9500 Mc/s in the planes Z-x, x-y, y-z of the magnetic axes.

RESULTS

A. Oligoclase and microcline

The EPR spectra of Fe³⁺ in oligoclase and microcline are described by the following expression for the Spin Hamiltonien (W. Low and E. L. OFFENBACHER, 1965; M. M. ZARIPOV and L. JA. SHEKUN, 1964).

$$H = 1/3 b_2^0 O_2^0 + 1/3 b_2^2 O_2^2 + 1/60 b_4^0 O_4^0 + 1/60 b_4^2 O_4^2 + 1/60 b_4^4 O_4^4 + \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z).$$

The Spin Hamiltonien parameters are given in Table 1. ($\pm 1,0$ gauss for b_n^m and $\pm 0,01$ for g -factors.)

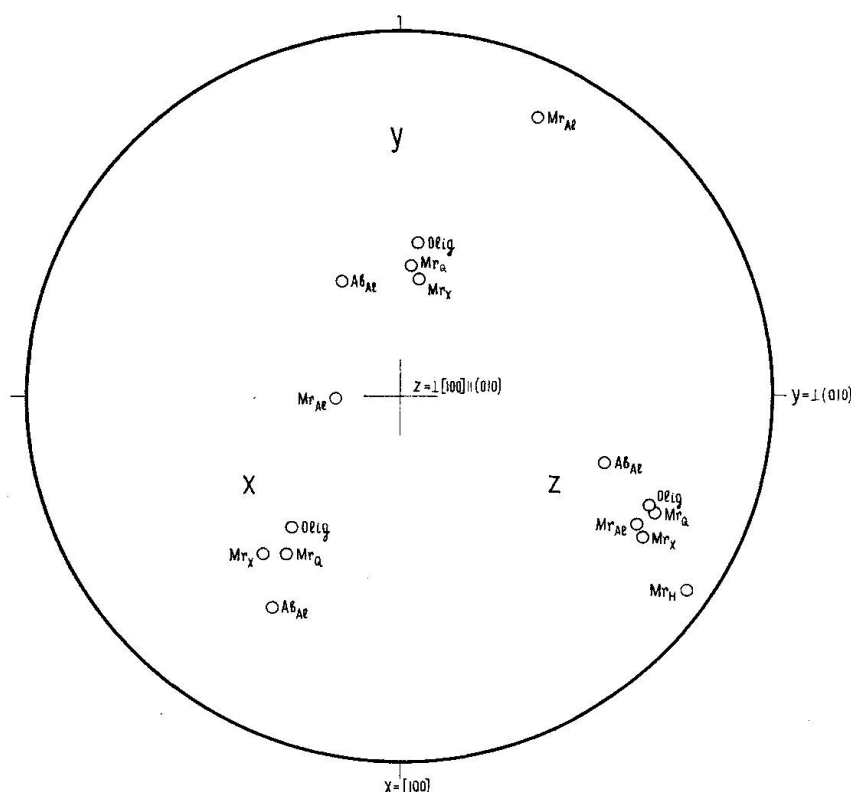


Fig. 4. Stereographic projection showing the orientation of the magnetic axes and of the principal axes of the electric field gradient.

Mr_Q-microcline, Khibin massiv, EPR, Q-band. Mr_X-microcline, Khibin massiv, EPR, X-band. Mr_H-microcline (U. HÖCHLI, 1964), EPR, X-band. Mr_{A1}-microcline, electric field gradient at Al-sites (ST. HAFNER and P. HARTMANN, 1965). Ab_{A1}-albite, electric field gradient at Al-sites (ST. HAFNER and P. HARTMANN, 1965). Olig-oligoclase, EPR, Q-band.

¹) The parameters obtained by U. HÖCHLI (1964) for Fe³⁺ in microcline are $b_2^0 = 1130$ gauss, $b_2^2 = 543$ gauss, $b_4^4 = 1500$ gauss. There is no description of this microcline.

Table 1. *Spin Hamiltonien for Fe³⁺ in oligoclase and microcline (gauss)*

	b_2^0	b_2^2	b_4^0	b_4^2	b_4^4	g_x	g_y	g_z
oligoclase	1927	383	9	10	25	2,001	2,001	2,005
microcline	1138	1198	6	17	75	2,00	2,00	2,00

The values of the energy levels for the three magnetic axes were calculated and plotted in Figs. 1 and 2. The observed Q-band and X-band transitions are shown. In addition to the "allowed" iron lines, there are also "forbidden" lines.

The calculated angular variation of the spectrum Fe³⁺ in oligoclase in the planes zy, yz, xz of the magnetic axes at X-band frequency is shown in Fig. 3.

Fig. 4 shows the direction of the magnetic axes, and table 2 gives the direction cosines with respect to a set of orthogonal axes: $a = [100]$, $b = \perp (010)$, $c = \perp [100] \parallel (010)$.

Table 2. *Direction cosines of the magnetic axes and of the principal axes of eQq/h*

		a	b	c	Method	Reference
Oligoclase	g_x	0,587	-0,493	0,643	EPR Q-band	This paper
	g_y	-0,697	0,073	0,713		
	g_z	0,388	0,871	0,301		
Microcline	g_x	0,692	-0,466	0,552	EPR Q-band	This paper
	g_y	-0,621	0,042	0,783		
	g_z	0,406	0,871	0,275		
Microcline	g_x	0,653	-0,569	0,503	EPR X-band	This paper
	g_y	+0,574	0,079	0,816		
	g_z	0,496	0,824	0,274		
Microcline	g_x	—	—	—	EPR X-band	HÖCHLI, 1964
	g_y	—	—	—		
	g_z	-0,57	0,82	0,07		
Microcline	V_{xx}	0,007	-0,356	0,934	NMR	ST. HAFNER and P. HARTMANN
	V_{yy}	0,888	-0,428	-0,170		
	V_{zz}	0,461	0,831	0,313		
Albite	V_{xx}	0,788	-0,488	0,375	NMR	ST. HAFNER and P. HARTMANN
	V_{yy}	-0,551	-0,288	0,783		
	V_{zz}	0,274	0,824	0,496		

A single site only of Fe^{3+} is found both in oligoclase and microcline. Two spectra of Fe^{3+} in microcline show the same relation as the microcline twins.

The linewidths are about 20 gauss for $-1/2 \rightarrow +1/2$ transition, 60 gauss for $\pm 1/2 \rightarrow \pm 3/2$, 80 gauss for $\pm 3/2 \rightarrow \pm 5/2$ both in oligoclase and microcline.

B. Low-sanidine ("Fe-orthoclase" from Madagascar)

At frequency 35.000 Mc/s only the $1/2 \rightarrow -1/2$ transition could be observed, but there are two magnetically inequivalent sites. The linewidths are very considerable: 100, 150 and 350 gauss for the principal directions (12475, 12485 and 12200 gauss).

CONCLUSION

The orientation of the g-factors obtained from this investigation was compared with the directions of the principal axes of electric field gradients available from the nuclear magnetic resonance investigation (Fig. 4).

The similarity of the positions of the z-axes in microcline, oligoclase and albite would seem to indicate that Fe^{3+} is located at the Al-sites in the unit cell of the ordered feldspars. This leads, in other words, to the assignment of Fe^{3+} to the tetrahedral $T_1(0)$ sites. Changes from order to disorder are accompanied by random variations of the atom coordinates and by the consequent spreading of the directions of the magnetic axes. This gives rise to a broadening of the EPR-lines from about 20 gauss in microcline and oligoclase to 350 gauss in low-sanidine.

After the identification and calculation of the spectrum of Fe^{3+} in microcline, oligoclase and sanidine, many samples of feldspars were tested for Fe^{3+} using EPR at frequency 9500 Mc/s. Concentrations of 0, n – 0,00 n% of tetrahedral Fe^{3+} were observed in sanidines, orthoclases, microclines (white and red), amazonites, albites, oligoclases, labradorites, anorthites from different localities.

Thus, Fe^{3+} ions are shown to be common as substitutional impurities in feldspars and can be used for determining the composition, degree of order-disorder, and twinning in this group.

Further investigations of EPR of Fe^{3+} in feldspars are now in progress.

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