

Single Crystal Transfer Device and Rotation System for ESR Measurements

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A device has been designed for the transfer and rotation of single crystals so that angular dependent ESR data can be obtained with a stationary magnet and rectangular cavity. The apparatus consists of a modified Donnay optical analyzer and a second goniometer which is rotated about a vertical axis in the ESR instrument. It has been possible to transfer crystals within $\pm 0.5^\circ$ of the desired orientation. Measurements of effective g values on two systems yielded standard deviations of 0.001 or less.

INTRODUCTION

SOLID state studies of the electron spin resonance (ESR) spectra of metal ions and other centers are best interpreted by means of single crystal angular dependence measurements. A number of instruments have been designed for this purpose. (See Hutton and Seed¹ for the pertinent literature references.) They have been easily adapted to conventional ESR spectrometers which have rotatable magnets and large gaps between pole faces.

In our laboratory, ESR measurements are carried out on an instrument which utilizes a stationary NMR magnet designed for use at 40 MHz, with a concomitant narrow gap (3.8 cm). Therefore, angular dependence data had to be obtained by rotating the crystal. Also, because of the narrow gap it would be very difficult to position any devices close to the cavity itself. In view of these limitations, the experimental approach taken was to attempt to design an instrument which could be used to accurately transfer a crystal, aligned by optical and/or x-ray techniques, in a known orientation to a second goniometer. This would be suspended above the cavity and rotated to obtain the angular dependence measurements. The details of the design of the instrument and experimental data obtained on two crystals, which indicate the accuracy of the method, will be discussed.

I. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Crystal Transfer Device

The principal component of this system was an optical analyzer² which is normally used for optical alignment of transparent crystals mounted on the optic axis. The analyzer has a calibrated, rotatable vertical stage (comparable to the spindle axis of an x-ray diffraction unit) and a rotating horizontal stage. These provide two degrees of freedom relative to the crystal. Several components were added for the purpose of accomplishing the accurate transfer of the crystal to the ESR goniometer. Figure 1 presents a photograph of this device.

The ESR goniometer assembly was designed to provide lateral, vertical, and horizontal motion of the goniometer

relative to the fixed crystal. An exploded view of this assembly is depicted in Fig. 2.

The upper section (A), machined to close tolerances, was used to hold the shaft on which the ESR goniometer was mounted. This was fastened to a rack and pinion (B) which gave the lateral motion required for positioning the fiber of the ESR goniometer relative to the crystal. This assembly was attached to a base (C) which was positioned on an aluminum plate (fastened to the horizontal stage of the analyzer) by sliding it over a key (D). The key and plate were carefully located so as to insure an accurate alignment of the axes of both goniometers. A screw threaded through the plate provided vertical adjustment of the ESR goniometer assembly.

B. Experimental Procedure

The crystal was mounted with a water soluble glue on the x-ray goniometer. If it had well developed faces, initial alignment was done on an optical goniometer. Final alignment in all cases was by x-ray precession techniques.

When the crystal is transferred to the optical analyzer, it is necessary to have a precise knowledge of the orientation of the reciprocal and/or true axes of the crystal. This is easily accomplished by a suitable correlation between the spindle axes of the precession and optical analyzer instruments.

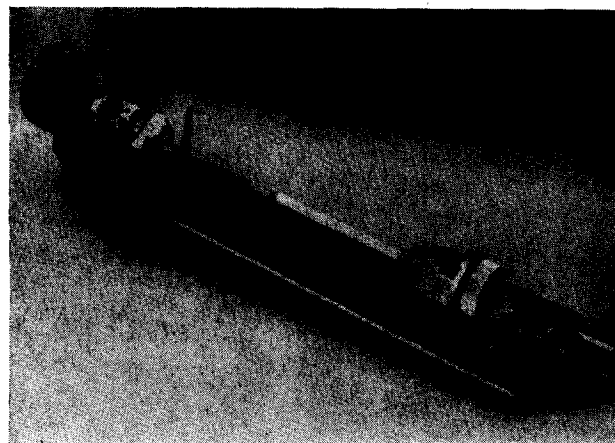


FIG. 1. Photograph of complete crystal transfer device.

¹ D. R. Hutton and T. J. Seed, *J. Sci. Instr.* **43**, 949 (1966).

² G. Donnay and J. D. H. Donnay, *Rev. Sci. Instr.* **28**, 145 (1957).

After both goniometers were properly positioned on the crystal transfer device, the ESR fiber, with an organic base glue on it, was brought into contact with the crystal. After drying, a drop of water was put on the water soluble glue and, within a few minutes, the transfer was complete.

C. Crystal Rotation System

An aluminum plate, with a scale graduated in 1° divisions fastened to it, was suspended above the magnet. A collar was mounted under the plate to prevent lateral movement of the goniometer and the plate was carefully leveled to insure that the goniometer rotated about a vertical axis.

The transferred crystal was put on a goniometer mount which had a longer shaft than the one used on the transfer device. The shaft had a scribe mark which was collinear with the positioning key of the mount. This system was suspended from the plate and held in a vertical position by a locking collar which also had a scribe mark collinear with the indicating pointer mounted on it. Therefore, from a knowledge of the orientation of the ESR goniometer relative to the real and/or reciprocal cell axes of the crystal on the crystal transfer device and by matching the scribe marks, a precise estimate of the position of the axes relative to the magnetic field direction was obtained.

Because of the narrow gap and presence of some magnetic parts on the ESR goniometer, it was necessary to position it 17.8 cm above the cavity. Initially, a long glass fiber was used for the crystal mount on the ESR goniometer. This proved unacceptable because room vibrations were transmitted to the crystal which at times resulted in detuning of the cavity. This was eliminated by using a nylon rod-glass rod combination (see Fig. 1) which provided a very stable situation.

II. EXPERIMENTAL RESULTS

This experimental technique has been used to obtain complete data on two crystals. The precision of the results

FIG. 2. Exploded view of ESR goniometer support assembly: (A) goniometer mount support; (B) rack and pinion for lateral motion; (C) base providing vertical motion; (D) positioning key for entire assembly.

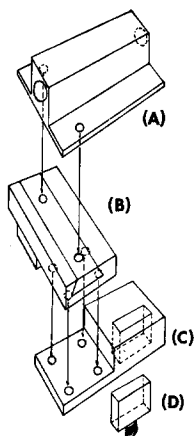


TABLE I. Test of accuracy of transfer of the Mn^{4+} -containing crystal.

Angle	$g_{\text{effective}}$
0°	3.9728
45°	3.9715
90°	3.9722
-45°	3.9748
-90°	3.9734

obtained, which clearly indicate the accuracy of this procedure, will be discussed below. The detailed analysis of the spectra will be published at a later date.

A. Mn^{4+} in Ammonium 9-Molybdonickelate (IV)³

A partial structure analysis⁴ of ammonium 9-molybdomanganate (IV), with which the nickelate (IV) is isomorphic, has shown that the Mn^{4+} occupies a site with space group demanded symmetry of $32(D_3)$, indicating that an axial ESR spectrum should be observed.

This was confirmed experimentally and further it was found that the magnetic z axis coincided with the crystallographic threefold axis. With this information, the accuracy of the procedure was tested by aligning, transferring, and rotating the crystal about the threefold axis. The perpendicular spectrum is observed in this orientation and g_{\perp} (taken as the mean of the two innermost lines of the six line hyperfine spectrum) should be invariant with respect to angular changes. The effective g_{\perp} 's obtained are presented in Table I.

The average value is 3.9729 with a standard deviation of 0.0013. In addition, the crystal was intentionally misaligned by making 1° changes in the arc settings of the ESR goniometer. New measurements showed that g_{\perp} effective changed significantly in the second decimal place when the crystal was rotated.

The crystal was realigned with the threefold axis along the spindle of the x-ray goniometer. The ESR goniometer was positioned perpendicular to the x-ray one and the crystal transferred. In this way, one obtains both g_{\parallel} and g_{\perp} . The value found for g_{\perp} was 3.9738 which was in excellent agreement with the previous value.

B. Fe^{3+} in $LiAlSiO_4$ (β -eucryptite)⁵

This mineral is a "stuffed" derivative of β -quartz (SiO_2) in which Al^{3+} is substituted for Si^{4+} , Li^+ being necessary for charge compensation. It was assumed that Fe^{3+} would substitute for Al^{3+} in the structure, and the ESR spectra justify this assumption. Since the β -quartz type structure belongs to the hexagonal system, a repetition of the ESR

³ K. M. Beem, E. J. Hornyak, and P. G. Rasmussen (to be published).

⁴ J. L. T. Waugh, D. P. Shoemaker, and L. Pauling, Acta Cryst. **1**, 438 (1954).

⁵ E. J. Hornyak, K. M. Beem, and P. G. Rasmussen (to be published).

TABLE II. Precision of Fe³⁺ fine-structure lines in β -cryptite.

Angles	g' av	$\sigma(g')$	B	$\sigma(B)$
0°, ±60°	2.7288	0.0003	2495.5 G	0.3
	2.3064	0.0005	2952.6 G	0.7
	2.2179	0.0003	3070.3 G	0.2
±30°, ±90°	3.0303	0.0005	2247.1 G	0.3
	2.6813	0.0005	2539.6 G	0.4
	2.3039	0.0003	2955.8 G	0.3
	2.1575	0.0005	3156.8 G	0.7

spectrum is observed every 60° when rotated about the crystallographic c (sixfold) axis.

The magnetic z axis coincides with the crystallographic c axis and, when rotated about this axis, maxima and minima in the g values are observed when true and reciprocal cell axes are parallel to the magnetic field. Thus, with the 60° repetition, an internal check is available for testing the accuracy of the mounting and transfer procedure.

The maxima and minima for a few of the lines were measured at several symmetry related orientations. The average effective g values (g') and the corresponding magnetic fields and their standard deviations are presented in Table II.

The largest absolute difference in g' values between any two of the individual measurements, for the lines which were fairly sharp and well resolved, was 0.001. The high degree of precision in the values indicates that a very accurate transfer had been obtained.

A more critical test of this procedure was provided by aligning, transferring, and rotating the crystal about an axis (a_2) which is perpendicular to the c axis. In this orientation, when c is perpendicular to the magnetic field, the spectrum is identical to that obtained at the 90° orientation when rotating about the c axis. The observed data for the two comparable orientations are given in Table III.

From the excellent agreement it is evident that this experimental equipment and procedure is capable of providing very accurate ESR data.

The two crystals discussed here are members of rather high symmetry crystal systems and it has happened that one or more of the principal magnetic axes have coincided with true and/or reciprocal cell axes. However, this does

TABLE III. Comparison of a_2 and c rotation $g_{\text{effective}}$ values at comparable orientations.

Angle	a_2 rotation		g'	c rotation (av value) B
	g'	B		
90°	3.0307	2246.8	3.0303	2247.1
-90°	3.0313	2246.4		
90°	2.6814	2539.6	2.6813	2539.6
-90°	2.6825	2538.4		
90°	2.3040	2955.4	2.3039	2955.8
-90°	2.3038	2955.7		
90°	2.1579	3156.6	2.1575	3156.8
-90°	2.1578	3155.7		

not limit the applicability of the procedure. From repeated observations on the above two systems, it has been found possible to position a magnetic axis within 2° of parallel to the magnetic field. With this degree of precision, together with the accuracy of transfer of the crystal, it would be possible to position reference axes of the crystal on the ESR spectrometer quite accurately with respect to the magnetic field. Thus, it should be possible to study the angular dependence of the spectra of lower symmetry systems and deduce the directions of the principal magnetic axes relative to the orthogonal system of rotation axes which had been chosen. With the number of degrees of freedom of the crystal transfer device, the crystal could be transferred directly on a magnetic axis and the accuracy of the determinations checked.

The precision of the data obtained on the two systems studied indicates that a crystal can be transferred to within ±0.5° of the desired orientation. It also is evident that the crystal transfer technique and the procedure described for obtaining angular dependence data with a narrow gap, stationary magnet has proven to be very satisfactory.

There are several additional advantages of this system. Because the magnet does not rotate, cavity-enclosed modulation coils can be used. Cavity-enclosed coils allow high field modulation frequencies (e.g., 100 kHz) and correspondingly good spectrometer sensitivity. A second advantage is that crystal rotation does not detune the spectrometer since the goniometer is completely outside the cavity. Finally, the normal cavity accessories for temperature control using exchange-cooled gas may be retained.