Turkish Journal of Physics

Volume 27 | Number 4 Article 5

1-1-2003

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Recommended Citation

ULUSOY, ÜLKÜ (2003) "ESR Studies of a Quartz Single Crystal from the Menderes Massif-Turkey," *Turkish Journal of Physics*: Vol. 27: No. 4, Article 5. Available at: https://journals.tubitak.gov.tr/physics/vol27/iss4/5

Turk J Phys
27 (2003) , 263 – 269.
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ESR Studies of a Quartz Single Crystal from the Menderes Massif-Turkey

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Received 17.06.2002

Abstract

In a recent work, quartz single crystal extracted from the pegmatitic vein in the Menderes Massif (Western Turkey) was investigated and the most recent geological events of the sample was dated using Al centers by ESR (electron spin resonance) techniques. The estimated age of 1.8±0.5 My agree with neither the previous age evaluated to be 12 My by using isotopic dating techniques nor the lifetimes of these centers in the sample. It was suggested that the thermal or geothermal stressing history of the metamorphic region must have changed the apparent ESR age several cycles in this period. The other possibility should also be considered that annealing and reirradiation processes repeated for many times over a long period might effect the paramagnetic characteristics, such as g (spectroscopic splitting factor) values, hyperfine structures of the centers as well as change the ESR ages. Hence the motivation should be investigated at least one cycle.

In this study, the angular dependence of the ESR spectra of these centers has been surveyed to understand the influence of heating and reirradiation. Only g values of the Ti centers measured at 100 K could be investigated since their hyperfine structure was well-resolved, while the ESR spectra of Al centers were too complex for this investigation. The principal values and direction cosines of the g-tensor of the Ti centers were calculated to be nearly the same for natural, irradiated and irradiated-annealed-reirradiated samples. Ti centers destroyed by annealing were recreated by γ-reirradiation, at least for one step, without affecting the behaviour of the angular dependence of g.

Key Words: Electron Spin Resonance (ESR), dating, quartz single crystal.

1. Introduction

Quartz can be found abundantly in nature as single crystals or grains. It contains many interesting impurity and defect centers such as Al, Ti, Ge substituted for Si and E' formed either during growth or by subsequent irradiations [1].

ESR of the impurity centers in quartz has made possible the observation of the crystalline environment in the vicinity of the centers; and have allowed the identification of those ESR centers. For this reason, numerous impurity centers in quartz single crystal have been recognized by ESR. Weeks [2] investigated the temperature dependence values of the g tensor of E' centers of the quartz structure. Wright et al. [3] described Titanium "colour centers" in rose quartz. After Rinneberg and Weil [4] studied Ti^{3+}-H^{+} centers formed by X-irradiation using ESR, Isoya and Weil [5], Isoya et al. [1] and Bailey et al. [6] investigated uncompensated Ti^{3+}, TiO_4/Li centers and $[TiO_4]^{-}$, respectively, in quartz single crystal at low temperature.

Quartz in various geological materials have also been dated by ESR. ESR dating is based on the detection of paramagnetic centers produced by the natural radiation in minerals and accumulated over a geological time scale. The equivalent dose D_E for natural radiation is obtained by an additive dose and converted to age by assessing the annual dose D [7]. ESR dating of natural quartz have been carried out by Shimokawa et al. [8], Toyoda and Ikeya [9], Imai et al. [10] for volcanic rock, granite and volcanic ash, respectively. Yokoyama et al. [11], Falgueres et al. [12], Ulusoy and Apaydın [13] and Ulusoy and Ikeya [14] dated sediments and sepiolites, while Fukuchi et al. [15] and Ikeya et al. [16] used fault gauge sample for dating.

In a recent work, a large single crystal extracted from vein pegmatitic quartzite in the Menderes Massif (MM) was at first dated using Al and Ti centers in quartz via ESR [17]. However, the ESR age of the Al centers estimated to be 1.8±0.5 Ma does not agree with the previous age evaluated to be 12 Ma using isotopic dating techniques, while that of Ti can not be calculated due to saturation to irradiation doses.

After isothermal and isochronal annealing experiments, Ulusoy [17] calculated the life times of the Al and three lines of Ti at 15 °C ambient temperature as 84000, 2800, 160 and 16 years. In fact, the ESR age is an order of magnitude lower than the expected geological event for such minerals due to the short lifetime of paramagnetic centers at ambient temperatures, such as Al and the saturation of growth curve of the paramagnetic centers, such as Ti. One possible explanation for the apparent ESR age being much younger than the previously determined isotope dating age may be thermal alteration. The sample must have been subjected to such strong thermal alterations during the geological events, the ESR signal must have been reset to zero; and the thermal alteration must have repeated multiple times over 12 Ma. Thus, the present signal must have been produced after the last strong thermal alteration or, presumably, the most recent geological event.

So, the effects of the repeated treatments of annealing and re-irradiation over time, on the behaviour of these paramagnetic centers, should be investigated for at least one cycle.

For that purpose, doses of irradiation and heat treatment were applied to a sample from the MM and the subsequent changes in the angular dependence of the ESR parameters were investigated. The sample was subjected to irradiation, annealing and then re-irradiation, which would presumably simulate the natural regeneration of the dose response curves. Then, the angular dependence of g of the paramagnetic centers in natural, annealed and re-irradiated sample was compared with one another. Based on these data and ESR dating techniques, the age of the last possible geological event for the powdered sample could be ascertained.

2. Experimental Procedure

To perform these studies, a single large α-quartz single crystal was extracted from the pegmatitic quartzite vein in Beydağ mountain situated near the Ovacık village of Ödemiş, at the center of the MM in Western Turkey (Figure 1). The MM has received special attention since the beginning of this century because it is situated in an area of regional metamorphism. Valuable information about the metamorphic history of the MM has been summarized by various authors [18, 19].

A square prism with the volume of 2 x 2 x 3 mm^3 was cut out of the natural quartz single crystal with the volume of 1.8 x 1.5 x 2.5 cm^3 in the x, y and z directions, (Figure 2). The Cartesian axes x, y and z where $x \equiv a_1$, $z \equiv c$ and $y \equiv z \otimes x$, were used. Crystalographic axes a_1 (crystal twofold axes, oriented 120° apart, $a_i \perp c$, i = 1,2,3) and c were determined by the Laue x-ray method. The same crystal reference axes system was employed in previous publications [20, 6].

The natural single crystal was attached to a goniometer to allow rotations within the microwave cavity in three mutually perpendicular axes (x, y and z). Rotation data of ESR measurements was collected by 15° steps in a range of 180°, for each of three planes $\boldsymbol{H}//yz$, $\boldsymbol{H}//xz$ and $\boldsymbol{H}//xy$. The typical ESR spectrum of the natural single crystal, for $\boldsymbol{H}//y$ in Figure 3, shows two groups of paramagnetic centers: Al and Ti, a hole and an electron trapped in substitutional Al and Ti replacing Si.

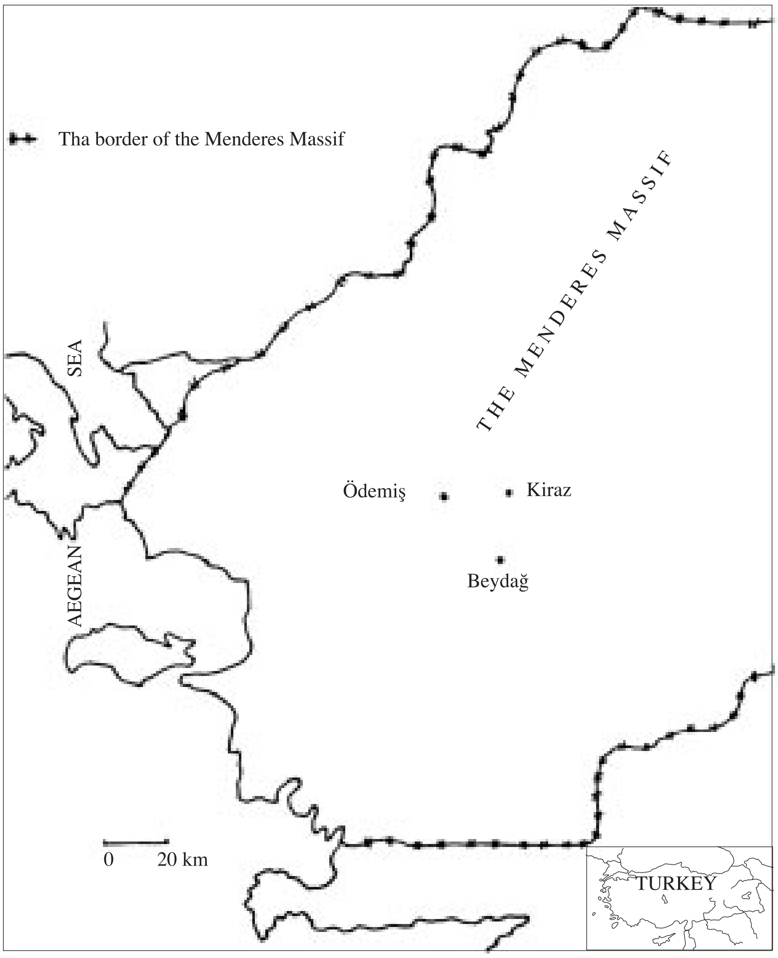

Figure 1. Generalized geological map of the Menderes Massif.

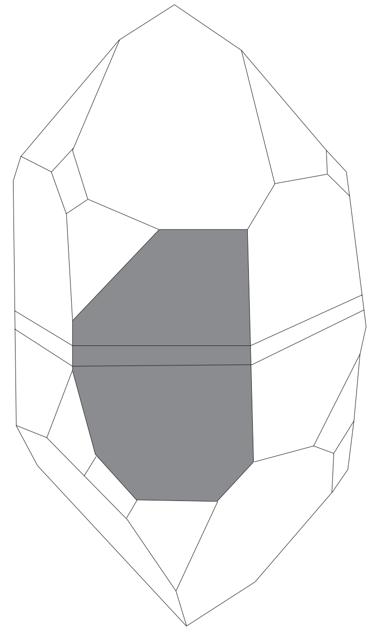

Figure 2. The investigated prism with the volume of 2 x 2 x 3 mm^3 cut out of the natural quartz single crystal with the volume of 1.8 x 1.5 x 2.5 cm^3. x-axis is normal to the shaded surface.

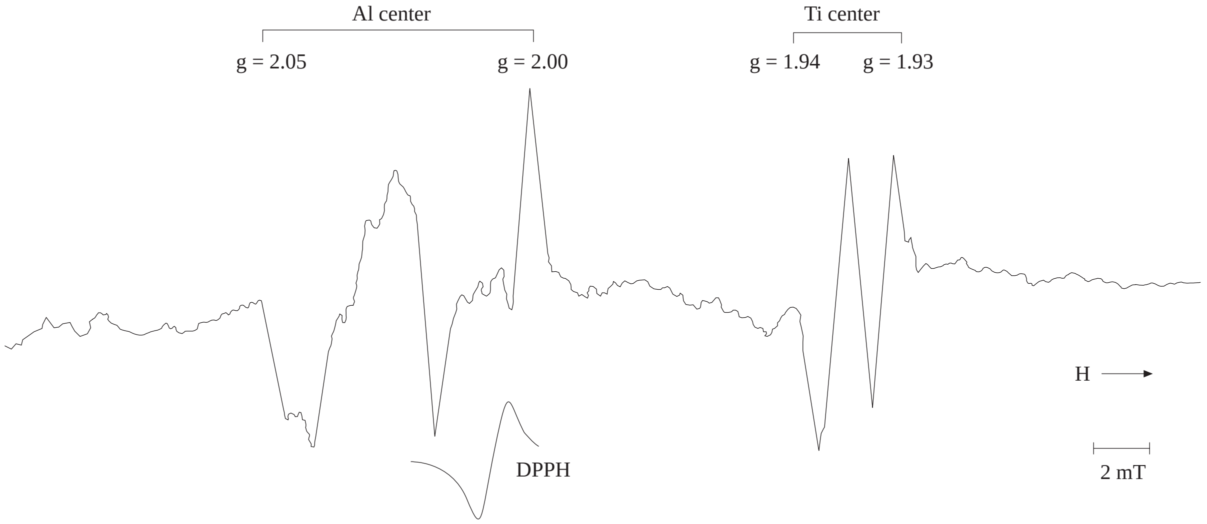

Figure 3. The ESR first derivative spectra of Al and Ti centers in the natural single quartz crystal at 100 K when $\boldsymbol{H}//y(\boldsymbol{H}$ is the applied external magnetic field).

In the second procedure, the sample was 2.3 kGy γ-irradiated by a ^{60}Co source at room temperature. The intensity of the Al centers increased much more while that of Ti did not change. There was no apparent new signal. Rotational data was collected for this sample. The γ-irradiated sample was annealed at 210 °C for 20 hours and then both Al and Ti signals were observed to disappear as experienced by Imai et al. [21] and Ulusoy [22]. In the last step, the sample was 2.3 kGy γ-reirradiated, with experimental data recorded. Thus, ESR data were recorded for natural, γ-irradiated and γ-irradiated-annealed-γ-reirradiated samples.

Data were collected at 100 K with a Varian E-L9 X-band ESR spectrometer operating at a frequency of around 9.35 GHz with 100 kHz modulation. Optimum experimental conditions during this work were the following: magnetic field value at resonance, 3250 mT; magnetic field scan range, 40 mT; amplitude of modulation field, 0.8 mT; magnetic field scanning time, 240 s; time constant, 1 s; microwave power, 90 mW; receiver gain, 2.5x10^3. The ^{60}Co source was used to irradiate single quartz crystal at a dose rate of 7.172 Gy/min at room temperature.

3. Results and Discussion

All ESR signals were observed to be spread over a large magnetic field varying from g = 2.00 to 2.07 and 1.93 to 1.97 for Al and Ti, respectively. Since virtually all Al sites have non-zero nuclear spins (^{27}Al, I = 5/2, 100% abundance), it might be expected that 2I + 1 = 6 equally spaced lines for Al centers. However, even at this simplest orientation, as shown in Figure 3, the actual spectrum is more complex than that expected due to nuclear Zeeman and Quadrupole splitting. On the other hand, the Ti center has revealed only two lines at this orientation.

At most orientations, Al and Ti centers showed poorly resolved hyperfine structures. For this reason, we could consider only the first term of the spin-Hamiltonian $\aleph$

$$\aleph = \beta_e \boldsymbol{S} \cdot \boldsymbol{g} \cdot \boldsymbol{H},$$

where β_e, $\boldsymbol{S}$, $\boldsymbol{g}$ and $\boldsymbol{H}$ are the electron magneton, total of electron spin operator, 3 x 3 Hamiltonian matrix of g and applied external magnetic field vector, respectively [23]. In this study, only the angular dependence of central g-factor (at the center of the first to the last line of the spectrum) for each Al and Ti of the sample in the magnetic field was investigated.

Final parameter values, the elements of matrix g^2, the principal values and direction cosines of matrix g for Ti, shown in the Table, were calculated using least squares fit computer program to repeatedly diagonalize the 3 x 3 matrix, while that of Al could not be resolved. The angular dependence of central g factor of Ti was found to be isotropic in the *yz* plane and anisotropic in the *xz* and *xy* planes for a natural sample, as shown in Figure 4 (H rotates from -y-, -x- and -y-axes ($\theta = 0°$) about x-, y- and z-axes, respectively).

In the second procedure, the γ-irradiated sample was investigated in the same way. Central g factor of Ti was isotropic in the *yz* plane and anisotropic in the *xz* and *xy* planes (Figure 5), while that of Al could not be resolved. Final parameter values of Ti in γ-irradiated sample were collected in the Table.

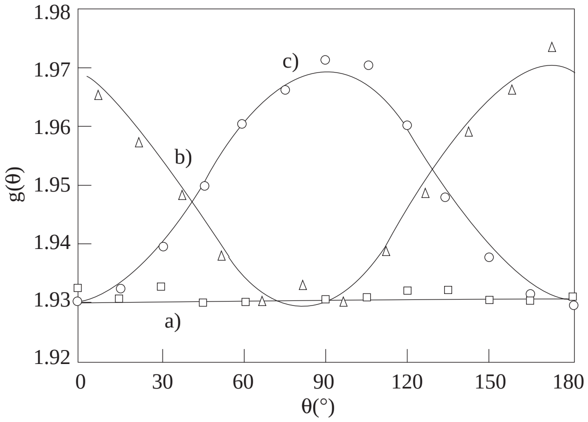

Figure 4. The angular dependence of ESR line positions of Ti center for the natural quartz single crystal. Rotation of the crystal about a) x- from -y-axis ($\theta = 0°$) b) y- from -x- axis ($\theta = 0°$) c) z- from -y-axis ($\theta = 0°$) (—: theoretical data; □, Δ, ○: experimental data).

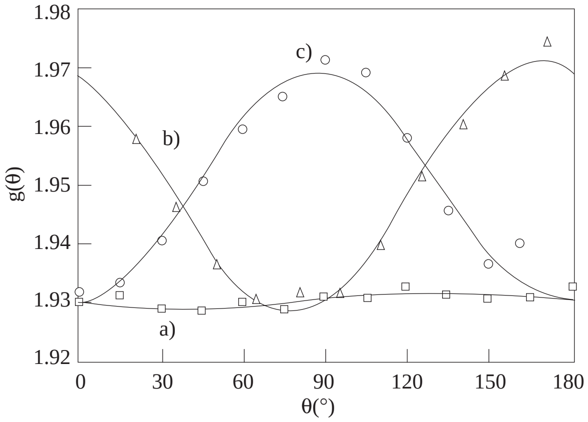

Figure 5. The angular dependence of ESR line positions of Ti center for the γ-irradiated single quartz crystal. Rotation of the crystal about a) x- from -y-axis ($\theta = 0°$) b) y- from -x-axis ($\theta = 0°$) c) z- from -y-axis ($\theta = 0°$) (—: theoretical data; □, Δ, ○: experimental data).

In the last procedure, the rotational data of the γ-irradiated-annealed-γ-reirradiated sample were recorded and evaluated to calculate the parameters same as natural and γ-irradiated sample. As shown in Figure 6, the angular dependence of signal positions of Ti in magnetic field looks quite a bit different from those in Figures 4 and 5. The elements of g^2, the principal values and direction cosines of matrix g were calculated as in the Table. Thus, all final parameters for natural, γ-irradiated, and γ-irradiated-annealed-γ-reirradiated samples were collected in the Table.

These investigations revealed that the principal values and direction cosines of matrix g for Ti center are almost the same for natural, γ-irradiated and γ-irradiated-annealed-γ-reirradiated sample. Our results are similar to those obtained by Bailey et al. [6]. They calculated principal values of the g matrix of Ti and found it exhibited only minor differences compared with the measurements at 30, 8 and 4 K. However, the angular dependence of central g-factor for the γ-irradiated-annealed-γ-reirradiated sample seems quite a bit different from that of the others. The origin of difference is not clear now, but certainly it is not from the possibly inaccurate mounting of the sample on the holder.

Table. The g^2 matrix, the principal values and the direction cosines of matrix g for Ti center in the quartz single crystal.

matrix g^2			**principal values of matrix g**	**direction cosines of matrix g**		
natural quartz single crystal						
3.8778	-0.0010	0.0228	1.9293	0.9894	-0.0049	0.1451
-0.0010	3.7274	0.0014	1.9308	-0.0365	0.9588	0.2817
0.0228	0.0014	3.7261	1.9701	-0.1405	-0.2840	0.9485
γ-irradiated quartz single crystal						
3.8752	-0.0066	0.0327	1.9279	0.9782	-0.0361	0.2047
-0.0066	3.7259	0.0037	1.9309	-0.0706	0.8684	0.4908
0.0327	0.0037	3.7267	1.9703	-0.1955	-0.4946	0.8469
γ-irradiated-annealed-γ-reirradiated quartz single crystal						
3.8746	0.0309	0.0356	1.9292	0.9537	0.2009	0.2237
0.0309	3.7339	0.0082	1.9307	-0.2306	0.9662	0.1156
0.0356	0.0082	3.7303	1.9722	-0.1929	-0.1618	0.9678

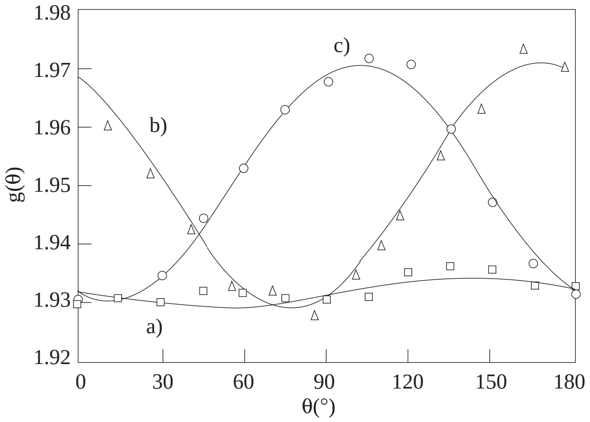

Figure 6. The angular dependence of ESR line positions of Ti center for the γ-irradiated- annealed-γ-irradiated single quartz crystal. Rotation of the crystal about a) x- from -y-axis ($\theta = 0°$) b) y- from -x-axis ($\theta = 0°$) c) z- from -y-axis ($\theta = 0°$) (—: theoretical data; □, Δ, ○: experimental data).

Ulusoy [17] calculated the ESR age of the Al in the same quartz single crystal from MM as 1.8 ± 0.5 My. This age does not agree with the age of 12 My calculated by using isotropic dating methods, indicating that the thermal or geothermal stressing history of the metamorphic region must have changed the apparent ESR age. So, the last metamorphic event should be accepted as 1.8 ± 0.5 My. However, the lifetimes for Al (8400 years) and the three lines of Ti (2800, 160, 16 years) are shorter than the ESR age of Al. This discrepancy can be explained in terms of the present day annual radiation dose from ^{238}U, ^{232}Th and ^{40}K being conventionaly much smaller than the previous annual doses under the severe environmental conditions, such as erosive, natural chemical etching and weathering processes. The age of Ti could not be obtained by ESR dating because the Ti centers were already saturated to γ-doses. So, the Ti centers can be said to have been annealed and irradiated repeatedly over the cycling times of, say, 2800 years since the last metamorphic events as indicated by the ESR dating of Al.

This research was carried out to survey the effects of the repeated treatments of annealing and reirradiation in nature, on the behaviour of the paramagnetic centers at least for one cycle. It showed that ESR parameters calculated by using rotational ESR data did not change for these procedures. We conclude that if a volume with Ti centers is completely annealed in a strong thermal events, it can be recreated and used for dating in the future.

Acknowledgements

I would like to thank Prof. Dr. Fevzi Apaydın (Hacettepe Univ. Dept. of Phys. Eng.) for his helpful comments, Prof. Dr.Seyfi Kulaksız (Hacettepe Univ. Dept. of Geo. Eng.) for providing quartz single crystals.

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