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Variable-temperature electron spin resonance of turquoise

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Abstract

The ESR spectra of several turquoise specimens contained an anisotropic component which was due to Cu^{2+} and an isotropic component arising from Fe^{3+} ions. The Fe/Cu concentration ratio obtained from these measurements agreed with ratios obtained analytically. A variable-temperature study from 77 K to 560 K indicated that the cupric ions are paramagnetic while the ferric ions behave antiferromagnetically at low temperatures.

Introduction

The magnetism of the hydrated copper aluminum phosphate mineral, turquoise, is mainly due to divalent copper ions. Previous papers (Diaz *et al.*, 1971; Poole *et al.*, 1977) presented an optical and electron spin resonance study of the copper ions in turquoise and interpreted the results in terms of the crystal structure (Cid-Dresdner, 1965). Many samples of turquoise also contain varying amounts of Fe^{2+} substituted for Cu^{2+} and Fe^{3+} substituted for Al^{3+}. We present evidence that these iron ions also make an important contribution to the magnetic properties of turquoise. We have studied the temperature-dependence of the Fe^{3+} and Cu^{2+} components of the ESR spectra, which exhibit an anisotropic part attributed to the copper ions and an isotropic part due to the iron ions.

Apparatus

The x-band (9.2 GHz) measurements in this paper were carried out with an Alpha ALX-10 ESR spectrometer in the temperature range from 77 to 560 K. Temperatures above and below room temperature, respectively, were obtained by passing heated or cooled nitrogen gas through the sample cavity. Electron microprobe data used in the analyses of the samples were taken with a scanning electron microscope, and the chemical analysis was carried out by Galbraith Laboratories.

Samples

Six different turquoise samples were obtained from Arizona, Nevada, New Mexico, and Virginia. They varied from 0.4 to 6 percent Cu and from 0.3 to 2 percent Fe. Many of the specimens showed wide variation in the content of copper and iron in different parts of the sample. The higher Cu/Fe concentration ratios were found in the bluish parts of the samples, and the lower ratios were in the greenish or brownish areas. As we will show, the relative concentrations of the copper and iron are directly related to the relative intensities of the anisotropic and isotropic lines, respectively, in the ESR spectra.

Variable-temperature spectra

The various samples produced ESR spectra which were superpositions of an unsymmetrical resonance arising from Cu^{2+} and a lorentzian-shaped singlet attributed to Fe^{3+}. Figure 1 shows two typical spectra decomposed into their components.

We have shown (Diaz *et al.*, 1971) that the Cu^{2+} resonance is a pattern arising from a completely anisotropic g tensor associated with a crystallographic site of C_i symmetry. The temperature-dependence of the spectral amplitude normalized relative to the commonly used ESR standard α, α' diphenyl β-picryl hydrazyl (DPPH) is shown on Figure 2 for one of the samples (Kingman, Arizona). Since DPPH is known to be paramagnetic, the horizontal plot of the copper

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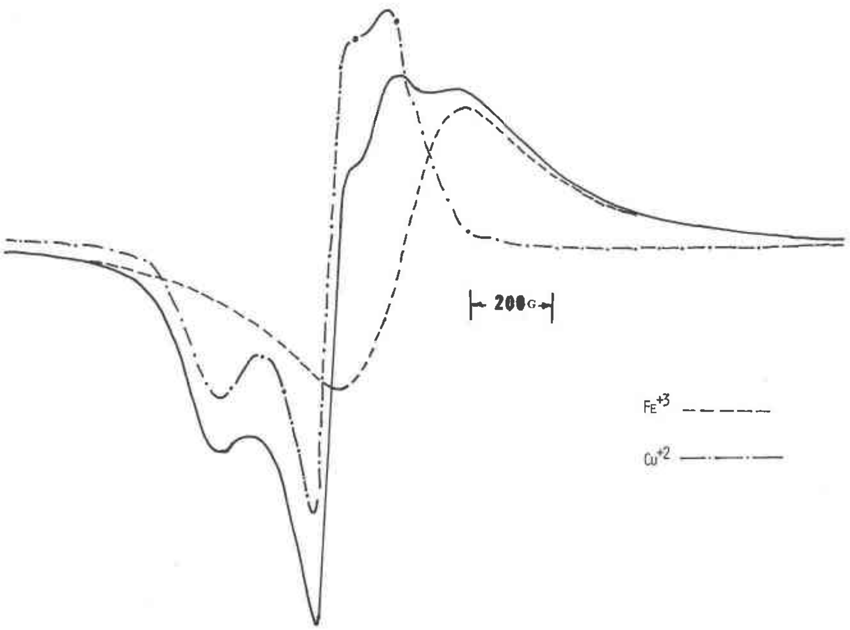

Fig. 1a. ESR spectrum of a turquoise from Kingman, Arizona, at 296 K resolved into copper and iron component lines.

data on this figure is indicative of a paramagnetic behavior of copper. The graphs of Figure 2 could not be continued to higher temperatures because of the chemical decomposition of the DPPH.

To clarify this variable temperature behavior of the iron signal, plots were made of the ESR amplitude ratio Fe/Cu normalized relative to the Fe/Cu ratio at 560 K for several samples. When the data were plotted in this manner all samples were found to follow the same empirical curve, as shown in Figure 3. Above about 400 K the plot of the data points became horizontal, corresponding to a typical paramagnetic behavior. At lower temperatures the amplitudes decreased, which may be indicative of anti-

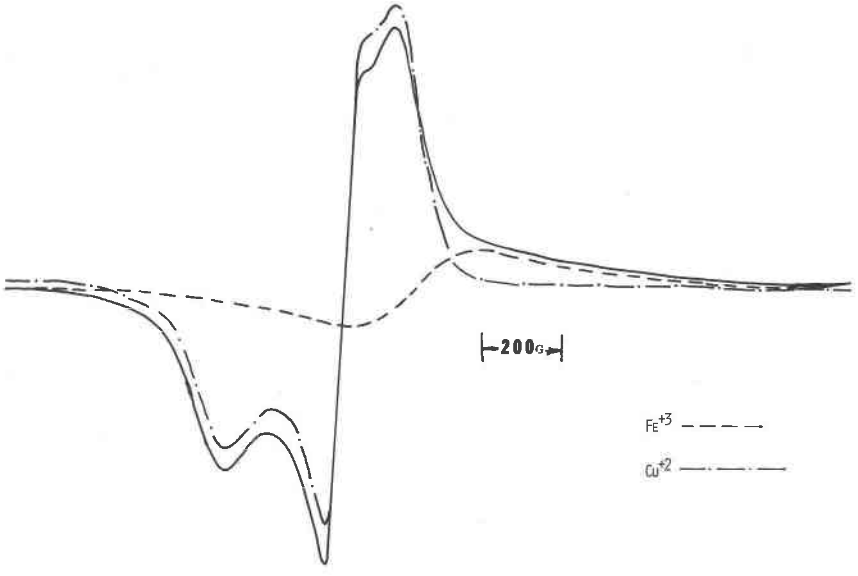

Fig. 1b. ESR spectrum of a turquoise from Kingman, Arizona, at 106 K resolved into copper and iron component lines.

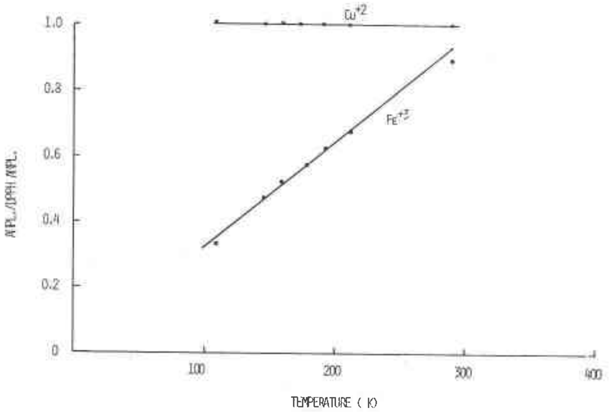

Fig. 2. Temperature-dependence of the ratio of component amplitudes to DPPH for the turquoise from Kingman, Arizona.

ferromagnetic behavior for one of the components, in this case Fe^{3+}. The fact that all samples have the same relative temperature-dependence leads us to conclude that the local coordination of Fe^{3+} may be the same in each.

Microprobe measurements

To confirm the origin of the isotropic line, the copper and iron contents of the various samples were determined both chemically and with an electron microprobe. Figure 4 shows the microprobe Fe/Cu ratios plotted against the amplitude ratios measured by ESR above 400 K. The best-fit least-squares straight line drawn through the origin fits the experimental points quite well, within the experimental errors indicated on the figure for both the microprobe and ESR measurements. The linearity indicates that the isotropic line is indeed caused by iron.

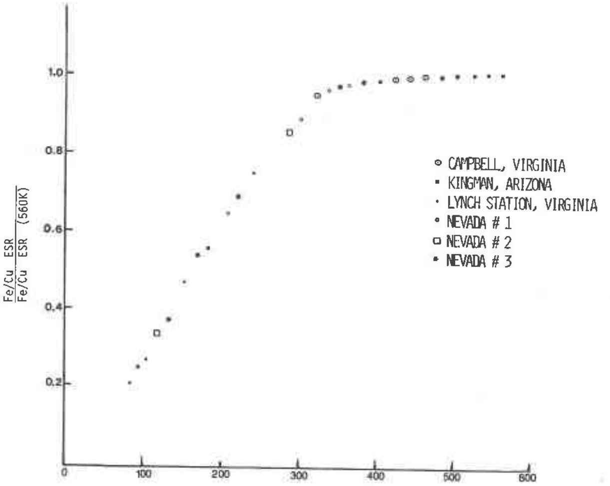

Fig. 3. Temperature-dependence of the ESR-determined Fe/Cu ratio normalized relative to the corresponding ratio measured at 560 K for turquoise samples.

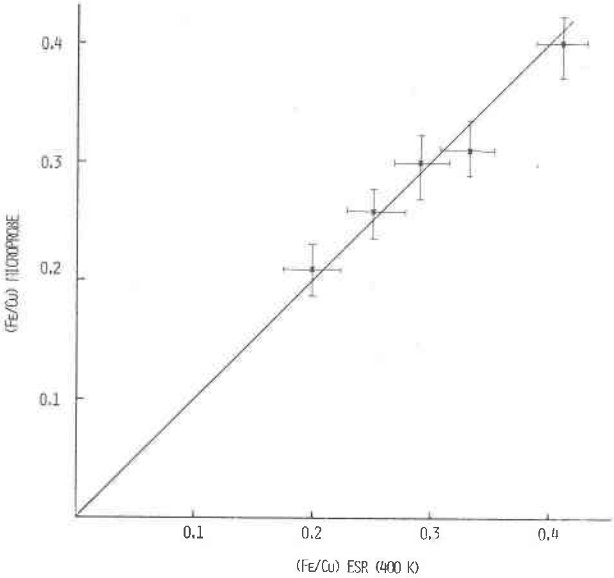

Fig. 4. Comparison of ESR iron to copper amplitude ratios at 400 K with microprobe iron to copper concentration ratios for turquoise samples.

Discussion

The ESR measurements indicated appreciable amounts of both iron and copper in all of the samples. The copper is in an ordinary paramagnetic state, while the iron ESR signal exhibits a temperature-dependence that may indicate antiferromagnetic behavior. Bluish parts of the specimens exhibited relatively stronger iron ESR signals, and greenish and brownish parts had weaker iron signals.

Acknowledgment

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