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Magnetic ordering in andradite

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Abstract

Andradite orders antiferromagnetically at 11.5±0.1 K. At 4.2 K the magnetic hyperfine field is 519±1 kOe. Mössbauer spectra taken in the magnetically ordered state consist of two sextets that have similar hyperfine fields and isomer shifts but different quadrupole splittings. Both sextets are commensurate with Fe^{3+} in sites that are crystallographically equivalent in the paramagnetic state. The existence of two sextets indicates that the sublattice magnetization and the electric field gradient are oriented along different directions.

Introduction

The structure of andradite, $Ca_3Fe_2(SiO_4)_3$, was first described by Menzer (1929) and later refined by Novak and Gibbs (1971). The space group of andradite, as that of other garnets, is *Ia*3*d*, and *a* = 12.058Å. Fe is located in the 16a position, and every Fe^{3+} ion is surrounded by six oxygens. These are arranged in the form of a slightly distorted octahedron, giving a symmetry of $\bar{3}$ for the Fe-sites. The shortest Fe–Fe distances are 5.221Å (parallel to [111]) and 6.029Å (parallel to [100]).

In the paramagnetic state the Mössbauer spectrum of andradite consists of a doublet with a quadrupole splitting ΔE_Q of about 0.55 mm · s^{-1} (Mill' et al., 1969; Dowty, 1971; Burns, 1972; Virgo and Huckenholz, 1974; Amthauer et al., 1976; Taran et al., 1978; Schwartz et al., 1980). Geller et al. (1964) predicted that andradite should order antiferromagnetically at about 9 K. Dodokin et al. (1973) gave approximate values for the Néel temperature as 10 K and the saturation hyperfine field as 550 kOe.

Experimental

The material used in this study is a demantoid of gem quality from Val Malenco, Italy. It is part of the original sample Parkin and Burns (1980) studied by optical spectroscopy (Harvard #87373). Microprobe analysis given by Parkin and Burns (1980) shows the sample to have the composition $An_{0.995}Gr_{0.003}Py_{0.002}$, i.e., to be almost pure andradite.

The garnet crystals were ground in an agate mortar and mixed with three parts sugar for Mössbauer spectroscopy. Sample quantities amounting to 5 mg Fe_2O_3/cm^2 were mounted in a Plexiglas holder for the Mössbauer measurements. The spectrometer comprised a ~25 mCi ^{57}Co/Rh source driven in a sinusoidal mode. Both source and absorber were cooled in a bath cryostat to 121±2 K using He gas as temperature exchange medium and to 4.2 K by immersion in liquid helium. All other spectra were taken with the absorber only cooled in a cold-finger cryostat. In this, temperatures were monitored with an Si-diode and kept constant to better than 0.02 K. Data were accumulated in a 1024 channel analyzer and processed (mirror halves folded, fitted with Lorentzians, and plotted) using a CDC Cyber 175 computer. The lines of the paramagnetic doublet and of corresponding pairs of the sextets were constrained to have equal intensities and widths. A 6 μm iron foil served as standard for velocity calibration and as isomer shift reference.

Results

At 121 K the Mössbauer spectra consisted of a paramagnetic doublet with ΔE_Q = 0.549 and δ(Fe) = 0.393 mm · s^{-1}. The quadrupole splitting is practically the same as that which Amthauer et al. (1976) found at 77 K for andradite from the same locality; apparent differences in the isomer shifts result from the fact that the spectrum described here was taken with both source and absorber cooled to the same temperature, whereas Amthauer et al. (1976) cooled the absorber only. Narrow lines of 0.236 mm · s^{-1} FWHM and an almost perfect fit by two Lorentzians indicate very little or no variation of the Fe^{3+}-environment.

A preliminary survey of the magnetic behavior in the vicinity by the Néel temperature was made by the thermal scan method with the source kept static, i.e., at zero velocity. Figure 2 shows that the absorption decreases quite abruptly by about 5% between 11.4 and 11.2 K. This is due to the paramagnetic doublet—the low-velocity peak of which lies near 0 mm · s^{-1}—being replaced by a sextet, which has no component at zero velocity, as the andradite orders magnetically. Figure 3 shows this behavior in Mössbauer spectra taken at 11.5, 11.4, and 11.3 K. At 11.5 K the line widths exceed those at 11.63 K (not

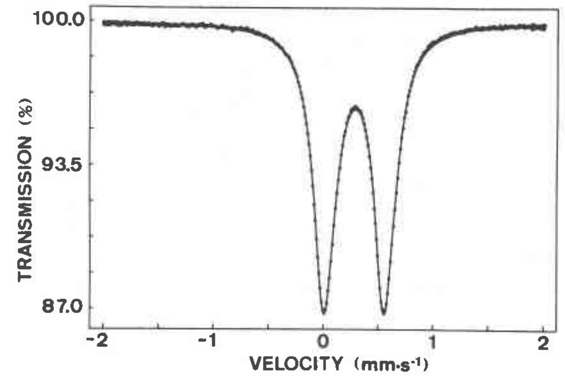

Fig. 1. Mössbauer spectrum of paramagnetic andradite at 121(2) K.

shown) by less than 0.01 mm · s^{-1}, and the spectrum is fitted quite well by two Lorentzians. At 11.4 K a two-Lorentzian fit gives lines that are wider than those at 11.5 K by more than 0.05 mm · s^{-1}. Increased absorption in the wings at the basis of the quadrupole doublet, which still makes up most of the 11.4 K spectrum, shows that magnetic ordering has already begun to take place. At 11.3 K the sextet structure of the magnetically ordered component begins to emerge, and the area under this sextet is almost twice as large as that under the remaining doublet (although the line profiles of the sextet still deviate noticeably from Lorentzian shape).

Below about 11 K the spectra can be fitted with two sextets. Magnetic hyperfine fields, calculated from the Mössbauer spectra, increase from an average of 270 kOe at 10.5 K to 519 kOe at 4.2 K, but the fields observed at any one temperature are always identical within the limits of experimental error. In contrast, the quadrupole splittings of the two sextets differ strongly, although their relative magnitudes and the relative intensities of the sextets appear to remain unchanged throughout this temperature range. Mössbauer parameters at 121 K (Fig. 1) and 4.2 K (Fig. 4) are given in Table 1.

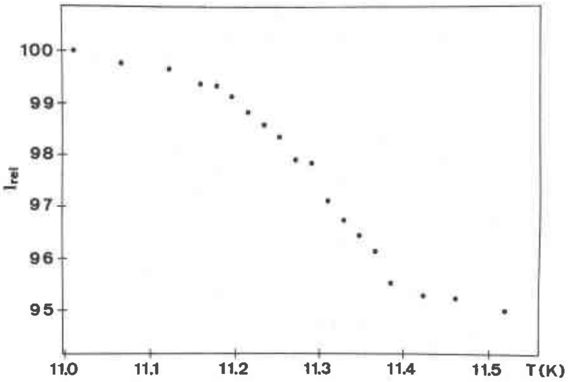

Fig. 2. Temperature-dependence of 14.4 keV γ-ray absorption for andradite in the vicinity of the Néel temperature.

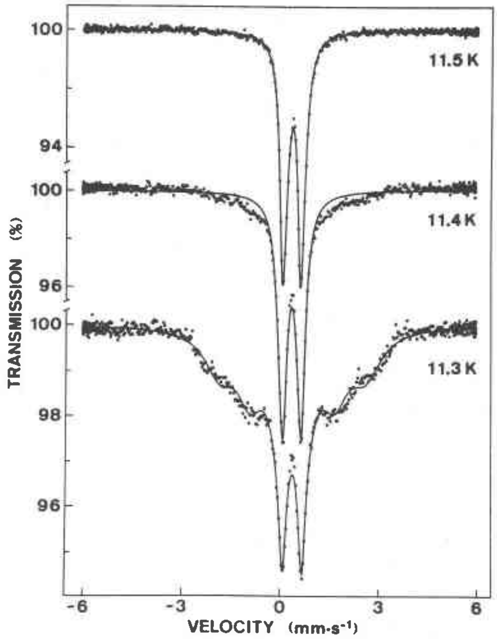

Fig. 3. Mössbauer spectra of andradite in the vicinity of the Néel temperature.

Discussion

The most striking feature of the described Mössbauer spectra is that, in spite of the fact that the andradite structure has only one crystallographic Fe^{3+} site (which is supported by the observation of very narrow resonant lines in the paramagnetic state), Mössbauer spectra of magnetically ordered andradite consist of two sextets.

The quadrupole splitting in the paramagnetic state ($\Delta E_Q^p = eQV_{zz}/2$, where e is the proton charge, Q the nuclear quadrupole moment of ^{57}Fe, and V_{zz} the principal component of an axially symmetric electric field gradient) and that in the (antiferro-) magnetically ordered state (ΔE_Q^{af}) are related by the equation

$$\Delta E_Q^{af} = \Delta E_Q^p \cdot (3\cos^2\theta - 1)/2$$

where θ is the angle between the sublattice magnetization

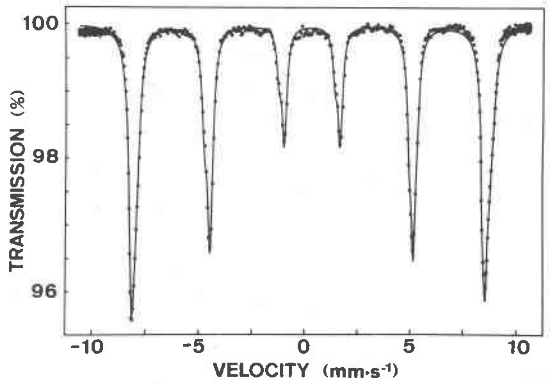

Fig. 4. Mössbauer spectrum of andradite at 4.2 K.

Table 1. Mössbauer parameters of the studied andradite (Harvard #87373) at 121 and 4.2 K

T(K)	Spectral component	δ(Fe)	ΔE_Q	FWHM	H_i	I_{rel}
			$mm \cdot s^{-1}$		kOe	
121	Doublet	0.393(1)	0.549(1)	0.236(1)	-	1.00
4.2	Sextet 1	0.378(3)	0.32 (1)	0.36 (1)	520(1)	0.29(1)
	Sextet 2	0.386(1)	-0.162(4)	0.352(6)	518(1)	0.71(2)

δ(Fe) = isomer shift relative to metallic iron
ΔE_Q = quadrupole splitting
H_i = magnetic hyperfine field
FWHM = full line width at half maximum
Numbers in parentheses give standard deviation on last digit.

and the principal component of the electric field gradient (EFG). The two sextets observed for magnetically ordered andradite at 4.2 K have quadrupole splittings of 0.32(1) and $-0.162(4)$ mm $\cdot$ s^{-1}, with relative areas of about 0.3:0.7. Solving the above equation for these quadrupole splittings shows that $eQV_{zz}/2$ is positive (Amthauer et al., 1976), and gives θ-values of 31.8(8) and 68.3(4)°, i.e., in this sample two angles exist between the magnetization and the EFG.

The EFG should be determined mainly by the oxygen octahedra surrounding the Fe^{3+}-ions (although the remainder of the lattice may play a role too). These octahedra are slightly distorted by flattening parallel [111], giving a symmetry of $\bar{3}$ for the Fe-sites. Because oxygen in the andradite structure is located in the general position *xyz* with $x = 0.03986$, $y = 0.04885$, and $z = 0.65555$ (Novak and Gibbs, 1971), the coordination octahedra of Fe^{3+} are oriented obliquely with respect to the crystallographic axes. This can be represented by an alternate rotation of these octahedra through opposite angles about their [111] symmetry axis (Geschwind, 1961).

If the EFG is oriented parallel [111], one of the following Mössbauer spectra should be observed in the magnetically ordered state for different simple directions of the magnetization: (1) one sextet with zero quadrupole splitting for a magnetization parallel to [100], or (2) two sextets of equal intensities and quadrupole splittings of 0.275 and -0.275 mm $\cdot$ s^{-1} for a magnetization parallel to [110], or (3) two sextets with splittings of -0.183 and 0.549 mm $\cdot$ s^{-1} and relative intensities of 1:3 for a magnetization parallel to [111].

The spectrum observed in the magnetically ordered state differs from all these cases. Provided the EFG remains axially symmetric in the magnetically ordered state and retains its direction (i.e., magnetostrictive distortions are negligible), andradite must possess a more complicated spin structure than those described above, which cannot be resolved by Mössbauer spectroscopy alone.

Extrapolation of the average magnetic hyperfine field observed at 4.2 K (519 kOe) to 0 K using a Brillouin function gives a saturation hyperfine field of 545±1 kOe.

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