Iron-57 Mössbauer Spectroscopy of Cr_2TeO_6 and Fe_2TeO_6

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Iron-57 Mössbauer spectroscopy has been used to determine the hyperfine field at a chromium site in Cr_2TeO_6 which is found to be 525 kOe. The Néel temperature for Cr_2TeO_6 containing 0.4% ^{57}Fe is found to be 90°K; the angle θ between V_{zz} and the magnetic axis is $42 \pm 4°$. These data are compared with those for Fe_2TeO_6 where H_{eff} $(T = 0) = 530$ kOe $T_N = 203°K$ and $\theta = 90°$.

Introduction

The tellurates containing iron and chromium, M_2TeO_6, (M = Fe, Cr) are isostructural being tetragonal with symmetry $P4_2/mnm$ (*1*). Neutron diffraction studies on iron tellurate, Fe_2TeO_6, has shown it to undergo antiferromagnetic ordering at a temperature of about 200°K (*2, 3*). Mössbauer spectroscopy was used to determine the transition temperature which was initially found to be $T_N = 218.5°K$ (*3*). Another study found that the ordering temperature for carefully purified samples was 201°K (*4*). A still later study of the magnetoelectric and Mössbauer properties identified the Néel temperature as 209°K (*5*). There is then considerable disagreement as to the actual Néel temperature, though those workers were in agreement as to the magnetic field at saturation which was given as 520 ± 10 (*3*) and 522 kOe (*4*) by the earlier groups. It is also claimed (*4*) that the quadrupole splitting, $\frac{1}{4}eQV_{zz}$ is negative and decreases slightly with decreasing temperature. The direction of the magnetic moment μ is believed to be parallel to the c axis of the crystal. The chromium analogue, Cr_2TeO_6, is also an antiferromagnet with an ordering

temperature of $T_N = 105°K$ (*2*), considerably below that of the iron tellurate. Here the magnetic moment lies perpendicular to the c axis.

In view of the uncertainty about the transition temperature for Fe_2TeO_6 and in order to establish beyond any doubt the Mössbauer parameters for this material a reinvestigation of this material seemed warranted. The chromium analogue has been doped with 0.4% ^{57}Fe and Mössbauer spectra recorded at a variety of temperatures in order to establish the transition temperature. Néel temperatures of 203°K and 90°K were found for Fe_2TeO_6 and $Cr_2(^{57}Fe)TeO_6$ with saturation fields at $T = O$ of 530 and 525 kOe respectively.

Experimental

Preparation of Compounds

Fe_2TeO_6 was prepared by grinding together equimolar quantities of Fe_2O_3 and TeO_2. The mixture was pressed into a pellet, placed in an open silica crucible in a muffle furnance, the temperature of which was raised to 700°C over a period of 24 hr. This temperature was maintained for a further

24 hr after which the sample was allowed to cool, reground and refired at 700°C. This latter procedure was continued until the X-ray powder diffraction pattern showed only lines due to Fe_2TeO_6 and the ^{57}Fe Mössbauer spectrum showed no lines due to Fe_2O_3 (see Fig. 1a). Heating of the compound at temperatures much above 700°

resulted in loss of tellurium and the appearance of Fe_2O_3 peaks. The previous workers claim to have prepared this compound by firing in air at 800° (3, 4, 5) but this procedure does not appear to be satisfactory.

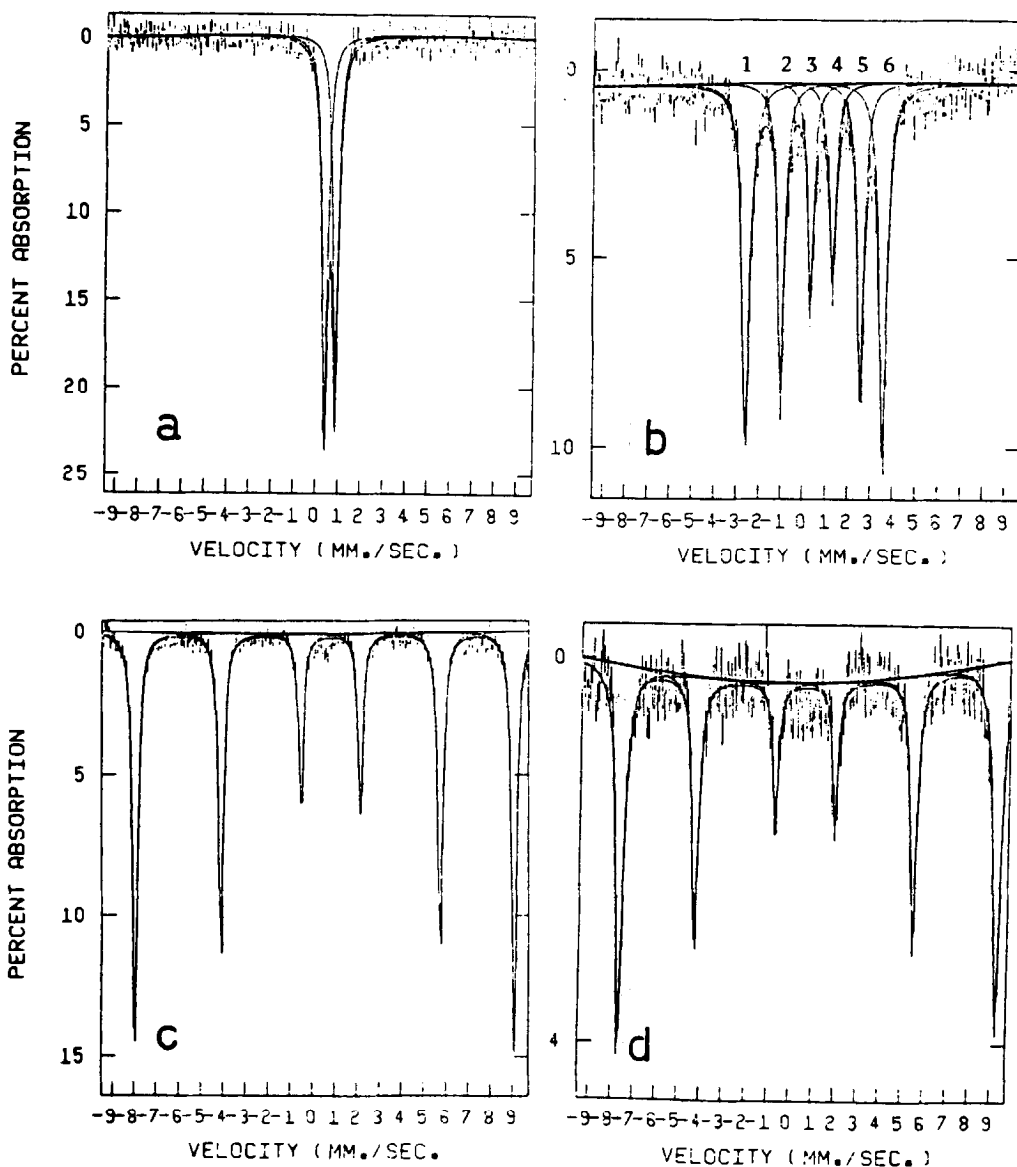Cr_2TeO_6 containing 0.4% ^{57}Fe was prepared in the same way using Cr_2O_3 which had

FIG. 1. ^{57}Fe Mössbauer spectra of (a) Fe_2TeO_6 at 298°K, (b) Fe_2TeO_6 at 200°K (c) Fe_2TeO_6 at 6°K, (d) Cr_2TeO_6 containing 0.4% ^{57}Fe at 6°K.

been previously doped with 0.4% $^{57}Fe_2O_3$ (6). Again the mixture was fired at 700° until no Cr_2O_3 or Fe_2O_3 lines were visible in either the powder pattern or Mössbauer spectrum: Cr_2O_3 containing 0.4% $^{57}Fe_2O_3$ shows a hyperfine field at 298°K and is easily detected (6). This hyperfine field in the Mössbauer spectrum appears after firing at 800° and again shows that preparation at 800° will result in impure samples. This is undoubtedly the reason for the lack of agreement among the previous groups who studied the Fe_2TeO_6 system.

Mössbauer Spectra

The Mössbauer spectra were recorded using an Elscint AME-40 drive system operating in the constant acceleration mode with automatic folding of the triangular waveform. The source was ^{57}Co in Rh obtained from Amersham–Searle and was maintained at room temperature. The transmitted radiation was detected by a Kr–CO_2 (1 atmosphere) proportional counter and the signal fed to the amplifier and single channel analyzer of a Tracor–Northern multichannel analyzer operating in the up-down multiscaling mode. Samples were finely ground powders, intimately mixed with apiezon grease and sandwiched in a copper holder between thin aluminum foils. These samples contained ~8 mg natural iron cm^{-2} or equivalent and were rigidly held in a Liquid Transfer Cryotip system manufactured by Air Products and Chemicals Inc., which allowed spectra to be recorded at liquid helium temperatures up to room temperature. Temperatures were monitored by means of a calibrated iron-doped gold chromel thermocouple and monitored by a Hewlett Packard 419A DC null voltage detector. In all cases spectra were computer fitted using the program written by Dr. A. J. Stone (7) and modified by Dr. D. H. Grundy of the Department of Geology, McMaster University. The instrument was calibrated using a standard iron foil and all chemical

isomer shifts were referenced to the center of this spectrum as zero velocity.

Results

The Mössbauer data are summarized in Table I and some representative spectra are shown in Fig. 1. Both Fe_2TeO_6 and the ^{57}Fe doped Cr_2TeO_6 show typical quadrupole split doublets above the Néel temperature (Fig. 1a) with chemical isomer shifts (δ) of 0.40 mm s^{-1} and quadrupole splittings (ΔE) of ~0.5 mm s^{-1}. The quadrupole splitting

$$\Delta E = \frac{eQV_{zz}}{2}\left(1+\frac{\eta^2}{3}\right)^{1/2},$$

where $-e$ is the charge or the electron, Q is the nuclear quadrupole moment, V_{zz} is the negative of the principle component of the electric field gradient tensor and

$$\eta = \frac{V_{xx}-V_{yy}}{V_{zz}}.$$

Since V_{zz} is usually coincident with the highest fold symmetry axis of the crystal and since Fe_2TeO_6 and Cr_2TeO_6 have local D_{4h} symmetry, η will be zero, and $\Delta E = eQV_{zz}/2$. The values found for δ and ΔE are typical of Fe^{3+} in distorted octahedral environments and are similar to those found for αFe_2O_3 (8) and for the Fe_2O_3–Cr_2O_3 system (6). The isomer shift varies with temperature and this is due to the second-order Doppler shift (9).

Hyperfine Spectra

The paramagnetic quadrupole doublets broaden at the onset of antiferromagnetism on cooling. For Fe_2TeO_6 a simple doublet is observed at 205°K while magnetic ordering occurs at 203° ± 1 K (extrapolated value), in good agreement with the Néel temperature reported by Dehn et al. (4) of 201°K and lower than the values given by either Montmory et al. (3) or Buksphan and coworkers (5). A well developed hyperfine field is

TABLE I

^{57}Fe MÖSSBAUER DATA FOR $Cr_2(Fe)TeO_6$ AND Fe_2TeO_6

Compound	Temp. °K	δ	ΔE	ε	H_{eff} kOe	$\dfrac{H_{eff}(T)}{H_{eff}(0)}$	T/T_N	T_N °K
		mm s^{-1}						
$Cr_2(Fe)TeO_6$	6	0.48	—	0.09	523	1.0	0.07	90
	25	0.48	—	0.10	513	0.98	0.28	
	77	0.47	—	0.09	369	0.70	0.86	
	78	0.47	—	0.07	369	0.70	0.87	
	80	0.50	—	0.11	356	0.68	0.89	
	83	0.50	—	0.07	283	0.54	0.92	
	84.5	0.52	—	0.04	252	0.48	0.94	
	85.5	0.48	—	0.08	251	0.48	0.95	
	90	0.50	0.49					
	298	0.40	0.51					
Fe_2TeO_6	6	0.49	—	−0.13	528	1.0	0.03	203
	77	0.49	—	−0.13	503	0.95	0.38	
	78	0.49	—	−0.13	498	0.94	0.38	
	98	0.49	—	−0.13	485	0.92	0.48	
	101	0.48	—	−0.14	475	0.90	0.50	
	144	0.46	—	−0.15	413	0.78	0.71	
	162	0.45	—	−0.15	365	0.69	0.80	
	181	0.45	—	−0.15	302	0.57	0.89	
	198	0.44	—	−0.14	220	0.42	0.98	
	200	0.44	—	−0.14	190	0.36	0.99	
	202.5	0.44	—	−0.14	150	0.28	1.0	
	298	0.44	0.48					

evident at 200°K (Fig. 1b) which increase rapidly as the temperature decreases below the transition temperature. At liquid nitrogen temperature the field is 503 kOe somewhat lower than the previously reported value of 520 kOe (3, 4). This field increases slightly to 528 kOe at 6°K and extrapolation to $T = 0°K$ gives a field of 530 kOe typical of that for an Fe^{3+} compound.

The onset of antiferromagnetism follows in the same fashion for $Cr_2(Fe)TeO_6$ but at a much lower temperature. A Néel temperature of 90°K is found in this case. This is significantly lower than that found by Kunnmann et al. who reported $T_N = 105°K$ for pure Cr_2TeO_6 (2). It is possible that the 0.4% ^{57}Fe impurity in Cr_2TeO_6 has caused a lowering of the ordering temperature, but this could only be established by a more

extensive compositional study. The temperature dependence of the hyperfine field is plotted for both compounds in Fig. 2, where smooth development of H_{eff} is observed. The extrapolated H_{eff} ($T = O$) for $Cr_2(Fe)TeO_6$ is 525 kOe essentially the same as for Fe_2TeO_6. It is apparent from Fig. 2 that the magnetic ordering develops much more rapidly for $Cr_2(Fe)TeO_6$ than for Fe_2TeO_6 though of course the Néel temperature is lower.

Quadrupole Interaction

The quadrupole splitting observed above the Néel temperatures for these compounds is dominated by the magnetic effect at low temperatures. Nevertheless this quadrupolar interaction is visible in the magnetic spectra (Fig. 1b, c, d) and is particularly evident just below T_N when the hyperfine field is small
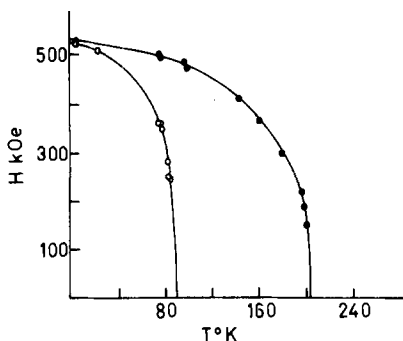
FIG. 2. Temperature dependence of the hyperfine fields for $Cr_2(Fe)TeO_6$ ○ and Fe_2TeO_6 ●. The drawn curves are visual fits to the data.
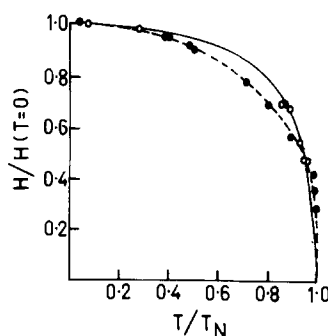
FIG. 3. Plot of $H_{eff}(T)/H_{eff}(T=0)$ vs. T/T_N for $Cr_2(Fe)TeO_6$ and Fe_2TeO_6 ●. The drawn curves are visual fits to the data.

(Fig. 1b). From the positions of lines 1,2 and 5,6 it is obvious that for Fe_2TeO_6 the sign of ε is negative:

$$\varepsilon = \frac{eQV_{zz}}{4} \frac{(3\cos^2\theta - 1)}{2} \quad (i)$$

where θ is the angle between the axis of magnetization and the direction of V_{zz}. The sign of this interaction, i.e. negative, is in agreement with that reported previously (3, 4). However in contrast to Dehn et al. (4) there is no significant change in the value of ε with temperature. Small changes from the average value of -0.14 ± 0.01 mm s^{-1} are within experimental error. In the case of $Cr_2(Fe)TeO_6$ the sign of ε is positive, its average value being smaller than for Fe_2TeO_6 at 0.08 ± 0.02 mm s^{-1}. Once again there does not appear to be any significant variation with temperature.

Discussion

Figure 3 shows a plot of reduced internal magnetic field $H_{eff}(T)/H_{eff}(T=O)$ vs. T/T_N for both the iron and chromium tellurate. There appears to be a slightly different temperature dependance for the antiferromagnetic ordering for the two systems. The near identical quadrupole splittings for Fe_2TeO_6 and $Cr_2(Fe)TeO_6$ of 0.48 and 0.49 mm s^{-1} respectively is expected from isostructural molecules and shows that this distortion arises from the lattice contribution to the electric field gradient. These values result in quadrupole coupling constants of $2\Delta E = 0.96$ and 0.98 mm s^{-1}. Since the average value of $4.\varepsilon$ for either system (-0.56 mm s^{-1} for Fe_2TeO_6, 0.32 mm s^{-1} for $Cr_2(Fe)TeO_6$) does not give the same value for eQV_{zz} as obtained above the Néel temperatures, it follows that the axis of the magnetic field is not coincident with V_{zz}. Furthermore the magnetic axes are oriented differently in the two compounds. Substitution of the experimental values in (i) results in a value of θ close to 90° for Fe_2TeO_6: in other words the magnetic axis is parallel to the crystal axis c, in agreement with previous findings (3, 4). For $Cr_2(Fe)TeO_6$, $\theta = 42 \pm 4°$ which is in contrast to that found for Cr_2TeO_6 where the magnetic axis lies in the basal plane and therefore parallel to V_{zz}. This disagreement with Kunnmann et al. (2) could be due to the effect of the 0.4% ^{57}Fe impurity in the Cr_2TeO_6 structure.

Acknowledgments

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