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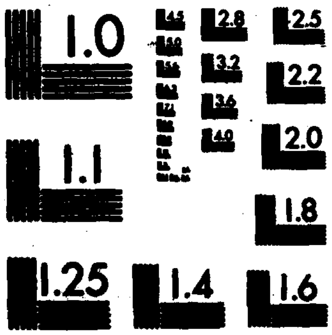

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Phase Transformation Study of Cu_2S.

by

John A. Gardner, D. K. Gaskill, M. Hirscher, H. Jaeger, K. S. Krane

and R. L. Rasera

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PHASE TRANSFORMATION STUDY OF Cu_2S

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The phase transformations of crystalline Cu_2S in the temperature range 50°C to 600°C have been studied through electric quadrupole interactions of ^{111}Cd impurities observed by time-differential perturbed angular correlations. The Cd is subject to no discernable quadrupolar interaction in the cubic phase above 430°C. In the hexagonal phase between approximately 103°C and 430°C, a single-site, weakly temperature dependent, axially symmetric quadrupolar interaction is found. At lower temperature, the structure is complex with a number of different sites. These data were taken with a microcomputer-controlled TDPAC spectrometer with logical steering that allows a standard 4-detector spectrometer to collect simultaneously 12 channels of data.

1. Introduction

The crystal structures of copper-sulfur alloys near the Cu_2S composition have been difficult to determine. There are a number of distinct Cu_xS compounds between x=1.8 and x=2.0. [1,2] For Cu_2S, the crystal structure of two high temperature phases has been measured, but the exact structure of the complex monoclinic room temperature unit cell is not known. [3,4] The phase transition from the "high chalcocite" hexagonal phase to the complex "low chalcocite" phase occurs at 103.5°C for x=2.000 but is reported to drop to 90°C for the slightly more sulfur-rich compound with x=1.990. [2] Supercooling of the higher-T phase by as much as 20°C has also been noted. [2,5]

In this experimental study, the time differential perturbed angular correlation (TDPAC) spectra of gamma rays emitted by dilute ^{111}Cd impurities in Cu_2S are measured. [6] The Cd atoms apparently enter the lattice substitutionally for Cu. Above 430°C, the lattice is cubic, and copper nuclei are in sites which have zero electric field gradient. As expected, the angular correlation of the gamma rays emitted by Cd nuclei is unperturbed in samples above 430°C. Between approximately 103°C and 430°C, the lattice is hexagonal, and the Cd TDPAC spectrum is typical of an axially symmetric quadrupole interaction. Below 103°C, th

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The phase transformations of crystalline Cu_2S in the temperature range 50°C to 600°C have been studied through electric quadrupole interactions studied through electric quadrupole interactions of ^{111}Cd impurities observed by time-differential perturbed angular correlations. The Cd is subject to no discernable quadrupolar interaction in the cubic phase above 430°C. In the hexagonal phase between approximately 103°C and 430°C, a single-site, weakly temperature dependent axially symmetric quadrupolar interaction is found. At lower temperature, the structure is complex with a number of different sites. These data were taken (ove

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with a microcomputer-controlled TDPAC spectrometer with logical steering that allows a standard 4-detector spectrometer to collect simultaneously 12 channels of data.

spectrum is complex and both time- and sample-dependent. It is clear that in order to attain good thermal equilibrium, the low-temperature samples should be annealed consideraby longer than the tracer decay time allows. Even though the equilibrium TDPAC spectrum cannot be readily measured in the room-temperature phase, the spectra of nonequilibrium samples provide some insight into its structure.

2. Experimental apparatus and procedure

Samples were made by sealing carefully weighed quantities of 99.999% purity copper and 99.99% purity S into quartz capsules, heating above the melting point of copper, and mixing for an hour or more before cooling. Since Cu_2S is reported to dissolve small amounts of sulfur but very little copper [2], samples were made very slightly Cu-rich. This was done to ensure that the sample was nearly stoichiometric Cu_2S with small inclusions of copper. The latter is cubic and more-or-less irrelevant in a TDPAC experiment. Approximately 0.05 cm^3 of this material was placed in a thin quartz sample capsule to which a few drops of ^{111}In/HCl solution were added. After drying, the capsule was sealed in vacuum and heated until the In had diffused well into the sample before any data were taken.

The TDPAC spectrometer consists of four NaI(Tl) scintillation counters arranged in fixed positions at 90 degree intervals in the horizontal plane around the sample furnace. Delayed coincidences of the two gamma rays are detected at interdetector angles of 90 and 180 degrees by a variation of standard fast-slow coincidence methods. Any counter can detect the first photon of the cascade and any of the other three can detect the second. The number of coincidences for any of the twelve possible counter pairs is counted, typically for 12 to 24 hours, as a function of time t between the two gamma emissions and stored in a microcomputer memory. Sample temperature is maintained by a small nichrome-wound water-cooled furnace.

Data are analyzed by forming the ratio

$$R'(t) = \frac{2}{3}\left\{\left(\frac{2\, C_{20}C_{31}C_{02}C_{13}}{C_{10}C_{21}C_{32}C_{03} + C_{30}C_{01}C_{12}C_{23}}\right)^{1/4} - 1\right\} \qquad (1)$$

$$R(t) \equiv A_{22}G_2(t) = R'(t)/[1 + 0.5R'(t)] \qquad (2)$$

where $C_{ij}(t)$ is the coincidence count rate when counter i detects the first and counter j the second gamma ray. Counters are numbered consecutively so C_{01}, C_{10}, C_{12}, C_{21}, etc. are 90° and C_{02}, C_{20}, C_{13}, and C_{31} are 180° coincidences. A more complete description of the spectrometer and data analysis methods will be published elsewhere.

Each type α of Cd site contributes a term,

$$R_\alpha(t) = A_{22}\left(S_0 + \sum_{i=1}^{3} S_i \cos(\omega_i t)\, e^{-(\omega_i t \delta)^2/2}\right) \qquad (3)$$

where the frequencies ω_i are determined by the electric field gradient (EFG), and the geometrical factors S_i depend on the orientation of the EFG principal axes. The damping parameter δ arises from the spread of frequencies in imperfect crystals. The complete R(t) is the sum of such terms, weighted by the probability of occurrence.

3. Experimental results and conclusions

In the hexagonal phase, R(t) could be fit to a slightly-damped single-site axially-symmetric quadrupole interaction. Typical R(t) spectra are shown in Fig. 1. Damping was somewhat sample-dependent and increased with decreasing temperature near the transition temperature. Damping may be due to slight departures from stoichiometry at low temperature where excess sulfur is soluble. The quadrupole frequency vs. T is given in Fig. 2.

Figure 1 also shows a typical R(t) for a sample below the monoclinic/hexagonal transition temperature. Monoclinic-phase spectra could not be well fit by either a single-site or 2-site interaction with moderate damping. A "2-site" computer fit in which one site was highly damped did describe the data reasonably well however. Approximately half the nuclei are in "good" sites having a quadrupole frequency ν_Q=119(6) MHz and asymmetry parameter η = 0.37(7). The highly damped portion apparently arises from nuclei in a number of different sites or from sites where the electric field gradient changes significantly during the data accumulation time.

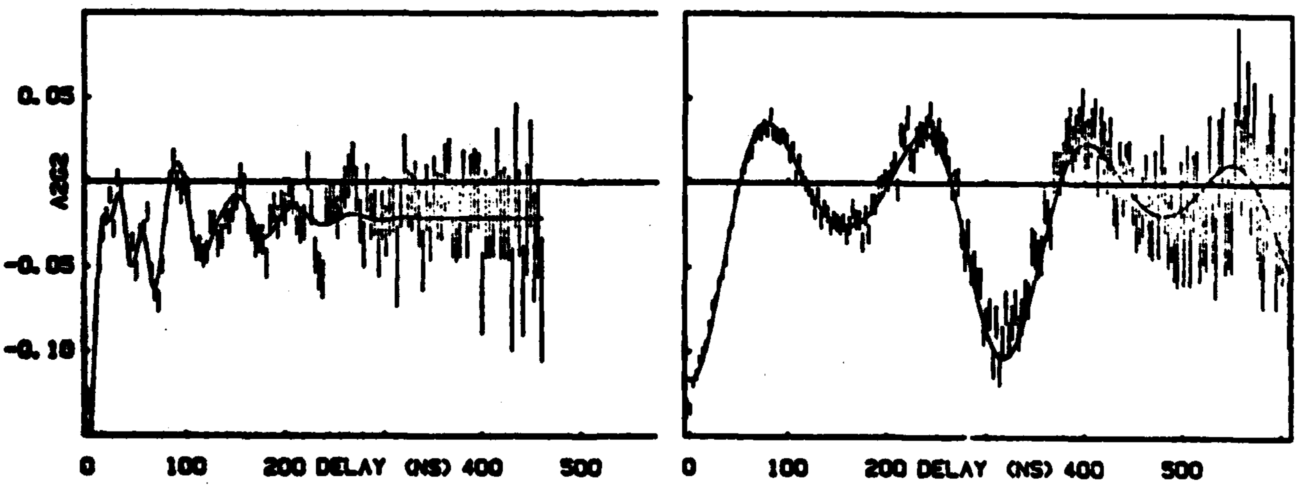

Figure 1. R(t) for dilute ^{111}Cd impurities in Cu_2S, hexagonal phase at 136°C (right) and monoclinic phase at 100°C (left). The full lines are computer fits to (right) a single-site axially symmetric quadrupolar interaction and (left) a 2 site model with one site subject to a slightly damped nonaxially-symmetric quadrupolar interaction, and the second "site" greatly damped.

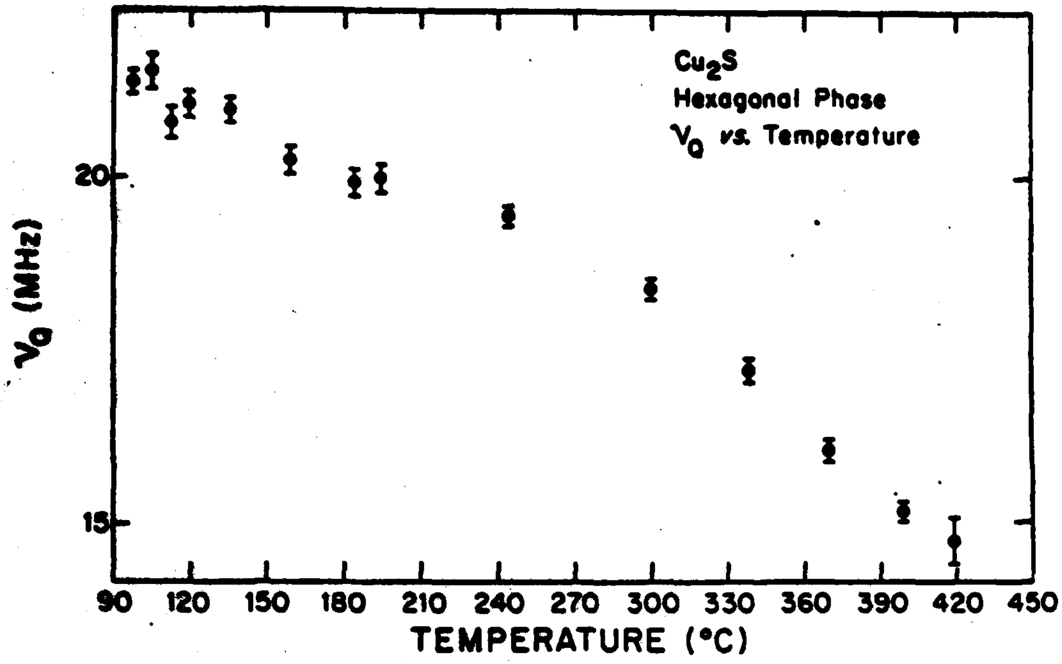

Figure 2. Quadrupolar frequency vs. T for ^{111}Cd impurities in hexagonal phase Cu_2S.

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