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Temperature-dependent nuclear magnetic resonance in $CuInX_2$ (X =S,Se,Te) chalcopyrite-structure compounds

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The NMR spectra of ^{63}Cu and ^{115}In in $CuInS_2$, $CuInSe_2$, and $CuInTe_2$ have been measured between room temperature and 550 °C. The effects of motional narrowing and of phase transitions on the shape and width of the absorption spectra were evaluated. In all three compounds, the absorption signal of ^{63}Cu shows motional narrowing. For $Cu_{1.00}In_{1.00}S_{2.00}$ the mean jump frequency of the Cu^+ ions, $\nu(Cu^+)$, is $2\times 10^{13}\exp[-(1.25\pm 0.10\text{ eV})/kT]\ s^{-1}$. For both $CuInSe_2$ and $CuInTe_2$, $\nu(Cu^+)$ is about $3\times 10^3\ s^{-1}$ at 350 °C. In copper-deficient $Cu_{0.96}In_{1.02}S_{2.00}$ no motional narrowing of the ^{63}Cu absorption was observed up to 550 °C. However, the ^{63}Cu line shape in $CuInS_2$ depends on the copper-to-indium ratio. A line-shape analysis as a function of composition shows that, at 450 °C, $CuInS_2$ exists in the composition range between $Cu_{1.00}In_{1.00}S_2$ and $Cu_{0.85}In_{1.05}S_2$. For specimens with $[Cu]/[In] > 1$, Cu_2S contributes to the absorption signal. In a separate study of the ^{63}Cu absorption in Cu_2S, the hexagonal-to-cubic transformation was observed at 440 °C. The activation energy for $\nu(Cu^+)$ in cubic Cu_2S is 0.15 eV. The phase-transformation temperatures for the three $CuInX_2$ compounds (where X is a group-VI element) were determined by differential thermal analysis. A previously unnoticed transformation was found in $CuInSe_2$ at 665 °C. Finally, the quadrupole coupling constant $\chi_q(^{63}Cu)$ of a number of $CuZX_2$ compounds (where Z is a group-III element) is shown to be a linear function of the tetragonal distortion parameter $\delta = 2 - c/a$ with $|\chi_q| = 1.50 + 90\delta$ MHz. The value for $\delta = 0$ is of the same order of magnitude as the result of a simple model of a point charge on a cubic lattice.

I. INTRODUCTION

Chalcopyrite-structure semiconductors of the type I*B*-III-VI$_2$ are analogs of the zinc blendes of type II-VI, in that the group-II atoms are substituted alternately by a group-I*B* and a group-III atom. This substitution leads to a doubling of the zinc-blende unit cell, by definition in the z direction. Because the electronic properties of group-I*B* and III atoms differ, real chalcopyrite structures do not conform precisely to the ideal quasi-zinc-blende picture. While the bonds of the group-III atoms remain essentially *sp* hybridized,[1] the bonding of the I*B* atom is strongly influenced by the participation of *d* levels. The *d* admixture results in a deviation of the free parameter x in the group-VI—atom $(x,\frac{1}{4},\frac{1}{8})$ from its ideal value $\frac{1}{4}$, as well as in a deviation of the unit-cell c/a ratio from its ideal value 2.00.

NMR spectra of I*B*-III-IV$_2$ compounds reflect nuclear dipole-dipole interaction as well as interaction of the nuclear quadrupole moments with the electric field gradients (EFG's) at the sites of the observed nuclei. The EFG is set up by the surrounding lattice, and by the electron system of the observed nucleus. Comparison of the EFG—in form of an experimental quadrupole coupling constant—with model calculations provides information concerning the charge distribution in the crystal and the chemical bonding of the observed atom. Additional information can be obtained from the chemical shifts of the absorption lines.

Quadrupole coupling constants for $CuInS_2$ have been reported by Peterson[2] and for $CuInS_2$ and $CuInSe_2$ by Spiess *et al.*[3] Becker and Schaefgen determined chemical shifts for $CuInS_2$, $CuInSe_2$, and $CuInTe_2$.[4] Spiess *et al.*[3] discussed the EFG's with a simple point-charge model whose shortcomings they admitted in view of the highly covalent character of the bonding in chalcopyrite-structure IB-III-VI$_2$ compounds. Lines[5] analyzed the bonding in these semiconductors with the bond-orbital theory and included both lattice and local orbital contributions to the EFG.

The nature of the point defects, electrically active or not, in these materials is not well understood. There is no lack of information about the apparent doping activity of impurities. However, interpretation and reproducibility of the doping experiments carried out to date are questionable in view of inadequate knowledge of the native point defects.[6] The potential for large concentrations of such defects exists because of the wide range of composition observed for nominally $Cu_{1.00}In_{1.00}X_{2.00}$ (where X is a group-VI element) stoichiometric compounds such as $CuInSe_2$ and $CuInTe_2$,[7] and $CuInS_2$ in our study. Peterson and Kasper[8] did employ NMR spectroscopy in an attempt to obtain information about $CuGaS_2$ crystals of different colors and lattice parameters arising from different compositions. These investigators observed reduced signal intensity and broadened lines for off-stoichiometric material.

We report the first study of the temperature dependence of the nuclear absorption signals of ^{63}Cu and ^{115}In in the chalcopyrite-structure CuInX_2 compounds. Our main results are the observation of motional narrowing arising from the diffusion of copper atoms and the detection of a stoichiometry-dependent absorption signal line shape in the pseudobinary system $(Cu_2S)_x(In_2S_3)_{1-x}$. In addition, we demonstrate the existence of a linear correlation between room-temperature quadrupole coupling constants of ^{63}Cu and the tetragonal distortion of the copper-containing chalcopyrite-structure compounds.

II. EXPERIMENTS AND EVALUATION OF DATA

Nominally stoichiometric CuInX_2 (where X is a group-VI element) crystals were prepared by reaction of either the elements or the binary Cu_2X and In_2X_3 compounds. The following high-purity elements were used: 99.999%-purity Cu (Demetron), 99.999%-purity In (Riedel de Haen), 99.999%-purity S (Fluka), 99.999%-purity Se (ICN Pharmaceuticals), and 99.999%-purity Te (Fluka). Zone-leveled crystals of $CuInS_2$ and $CuInTe_2$ were also investigated. The Cu and In concentrations in the ternary sulfide were determined by standard wet-chemical analysis.[9]

Derivative NMR absorption spectra of the powdered substances were recorded with a conventional cw wideline spectrometer. Measurements of ^{63}Cu and ^{115}In were performed at fixed frequencies of 16 and 13 MHz, respectively. The sample temperature was varied between room temperature and about 550 °C with a gas-flow system that had been fitted into the crossed-coil rf probe head.[10]

Both the ^{63}Cu (nuclear spin $I=\frac{3}{2}$) and the ^{115}In ($I=\frac{9}{2}$) nuclei possess magnetic dipole as well as electric quadrupole moments. The NMR absorption signals therefore are determined by the magnetic dipole-dipole interaction between the nuclei and by the interaction of the electric quadrupole moment with the electric field gradient at the nuclear sites. The line shape $g(B)$ of the experimentally observed absorption signal then depends on $g_b(B)$, a broadening function containing essentially the dipolar interaction, and on $g_q(B)$, the line-shape function characteristic of the quadrupole interaction.[11] The overall line shape $g(B)$ is given by the convolution of these two contributions[12]:

$$g(B)=\int_{-\infty}^{\infty} g_b(B-B')g_q(B')dB' , \tag{1}$$

where B is the magnetic field. We assume a particular shape, i.e., Gaussian, for $g_b(B)$. A computer-aided line-shape analysis[12] of $g(B)$ then produces the width of $g_b(B)$, ΔB_b, and the two parameters characterizing $g_q(B)$: the quadrupole coupling constant, $\chi_q=e^2qQ/h$, and the asymmetry parameter η (e is the electronic charge, $eq=V_{zz}$, the electric field gradient; Q, the nuclear quadrupole moment; and h, Planck's constant). The linewidth ΔB is defined as the spacing between the outermost inflection points (derivative extrema) of $g(B)$. ΔB is decomposed into ΔB_q of $g_q(B)$, and into ΔB_b of the Gaussian broadening function. In CuInX_2 compounds, the situation for such a deconvolution is favorable since ΔB_q and ΔB_b are of comparable magnitude. The nearly tetragonal symmetry justifies setting $\eta=0$, thus simplifying the relation between ΔB_q and χ_q to the following[11]:

$$\Delta B_q=\frac{25\pi}{8\gamma\nu_L}\left[I(I+1)-\tfrac{3}{4}\right]\left[\frac{\chi_q}{2I(2I-1)}\right]^2 . \tag{2}$$

γ is the gyromagnetic ratio of the nucleus under consideration, and ν_L is the measuring frequency. Hence, from line-shape analysis the absolute value—but not the sign—of the quadrupole coupling constant can be deduced.

Motional narrowing, as we observed in this study for ΔB_b(^{63}Cu), provides a measure of the mean jump frequency of the copper ions, ν:

$$\nu=2\gamma\,\Delta B_b\left[\tan\left[\frac{(\Delta B_b)^2-(\Delta B_r)^2}{(\Delta B_0)^2-(\Delta B_r)^2}\,\frac{\pi}{2}\right]\right]^{-1} , \tag{3}$$

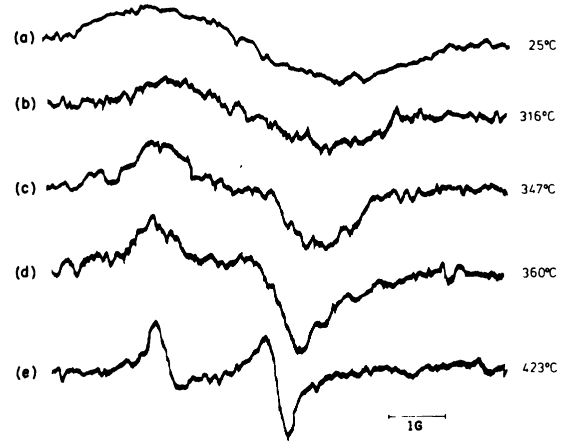

FIG. 1. NMR absorption spectrum of ^{63}Cu in stoichiometric CuInS$_2$ at five different temperatures; $\nu_L = 16$ MHz.

where ΔB_0 is the linewidth at temperatures below the onset of narrowing, and ΔB_r the residual width of the narrowed broadening function.[13] The temperature dependence of $\nu(\mathrm{Cu}^+)$ provides the activation enthalpy and the preexponential factor for the jump frequency. Neglecting details of the correlation between the successive jumps prevailing in NMR, we calculate the diffusion coefficient as $D(\mathrm{Cu}^+) = \frac{1}{6}\nu l^2$, where l is the jump distance. Assuming a substitutional diffusion mechanism with a jump distance equal to the nearest Cu-Cu distance, $l^2 = (a/2)^2 + (c/4)^2$.

III. RESULTS

A. ^{63}Cu in CuInS$_2$

Figure 1 shows the derivative absorption spectrum $g(B)$ of ^{63}Cu in stoichiometric CuInS$_2$ at five different temperatures between 25 °C and 423 °C. The signal changes from nearly symmetric at room temperature to one with pronounced fine structure. At 423 °C, and at higher temperatures, the line shape is that for an almost pure static quadrupole effect of second order.[11] Virtually identical behavior was observed for nominally stoichiometric samples prepared from the elements and from the binary compounds. The total linewidth ΔB is plotted as a function of temperature in Fig. 2 for the exactly stoichiometric sample Cu$_{1.00}$In$_{1.00}$S$_{2.00}$ (closed circles) and for a copper-deficient—excess-indium sample Cu$_{0.96}$In$_{1.02}$S$_{2.00}$ (open circles). Also shown are the deconvoluted dipolar (ΔB_b) and quadrupolar (ΔB_q) linewidths for the stoichiometric sample.

In the stoichiometric sample ΔB decreases only slightly from 2.7 G at room temperature to 2.6 G at 340 °C. Above 340 °C, pronounced narrowing—linear in temperature—is observed to a value of 1.7 G at 500 °C. The shape of the absorption signal, however, undergoes a dramatic change between 347 and 423 °C (Fig. 1). This change is due to a decrease

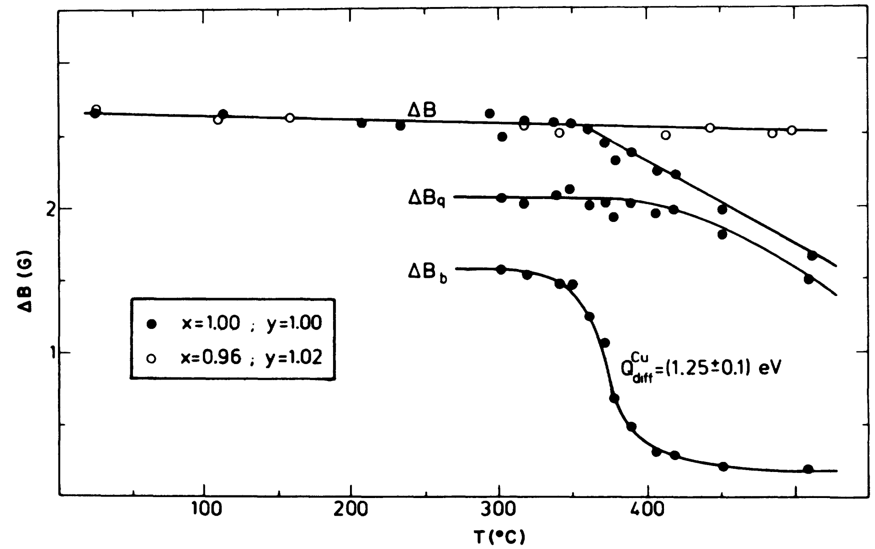

FIG. 2. Total (ΔB) ^{63}Cu linewidth and deconvoluted dipolar (ΔB_b) and quadrupolar (ΔB_q) linewidth for stoichiometric CuInS$_2$ (●). Total linewidth for a copper-deficient sample (○).

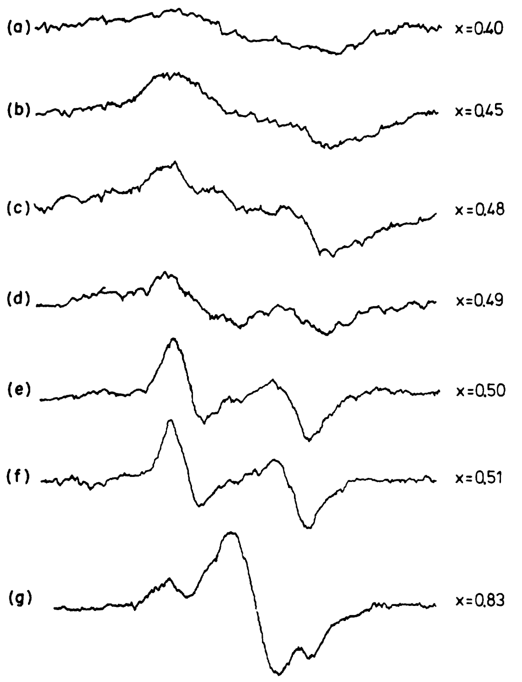

FIG. 3. NMR absorption spectrum of ^{63}Cu in the pseudobinary system $(Cu_2S)_x(In_2S_3)_{1-x}$ for different values of x at 450 °C; $\nu_L = 16$ MHz.

in the width ΔB_b of the broadening function from 1.4 G ($T < 300$ °C) to 0.2 G ($T > 450$ °C). The decrease results from motional narrowing due to diffusion of the spin-carrying copper ions. The diffusion averages out the dipolar contribution to the broadening function $g_b(B)$. We attribute the residual linewidth $\Delta B_r = 0.2$ G to relaxation lifetime broadening of the absorption analogous to that observed in the copper halides.[10,14] Accounting for ΔB_r (Eq. 3), the mean jump frequency of copper ions was calculated as

$$\nu(\mathrm{Cu}^+) \cong 2\times 10^{13} \exp[-(1.25\pm 0.10\ \mathrm{eV})/kT] \tag{4}$$

in units of s^{-1}. At 370 °C, the narrowing halfpoint of ΔB_b, $\nu(\mathrm{Cu}^+)$ is 3×10^3 s^{-1} corresponding to a diffusion coefficient $D(\mathrm{Cu}^+)$ of 8×10^{-13} $\mathrm{cm}^2\,\mathrm{s}^{-1}$.

The quadrupole coupling constant $\chi_q(^{63}\mathrm{Cu})$ of the stoichiometric sample varies little between room temperature and the onset of motional narrowing [see Eq. (2) and ΔB_q in Fig. 2]. The room-temperature value of 0.54 MHz, determined from ΔB_q [Eq. (2)], is in good agreement with that derived from the first-order quadrupole satellites (0.57 MHz). The decrease of ΔB_q above 400 °C provides evidence for the effect of ionic motion, of thermal expansion or contraction, or of both, on χ_q.

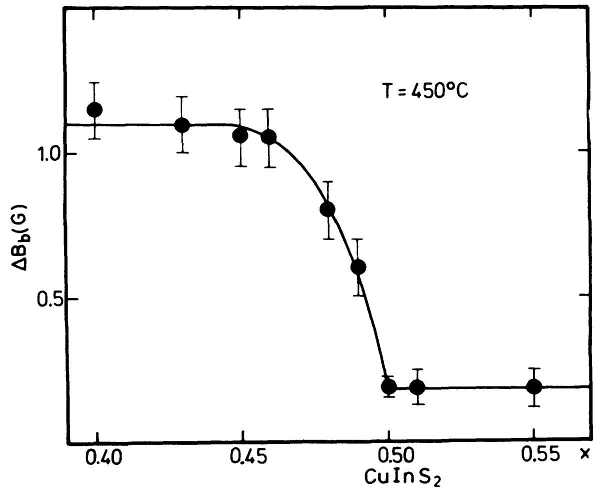

FIG. 4. Width of the broadening function, Eq. (1) for a range of compositions x in the system $(Cu_2S)_x(In_2S_3)_{1-x}$ at 450 °C; $\nu_L = 16$ MHz.

The ΔB values for the nonstoichiometric sample (open circles in Fig. 2) do not show motional narrowing. We investigated a wide range of composition, $0.40 \lesssim x < 0.83$ of the pseudobinary system $(Cu_2S)_x(In_2S_3)_{1-x}$ to clarify this unexpected observation. $x = 0.40$ corresponds to a nominal composition of $Cu_{0.73}In_{1.09}S_{2.00}$ and $x = 0.83$ to $Cu_{2.47}In_{0.51}S_{2.00}$ (or Cu_5InS_4).

At room temperature the absorption signals of ^{63}Cu in this pseudobinary system are of the nearly symmetrical shape shown in Fig. 1. However, the signal intensities do depend on stoichiometry and, particularly for $x = 0.40$ and 0.45, reduced intensities were measured. Figure 3 shows the absorption signals of ^{63}Cu for seven different compositions at 450 °C, which is well above the narrowing temperature in the stoichiometric sample. The spectra are affected strikingly by the sample composition. The line shapes for $x < 0.50$ display a drastic reduction in their fine structure with increasing In_2S_3 excess, resulting in an almost symmetrical signal for $x = 0.40$ and 0.45. In contrast, spectra for $x = 0.50$, 0.51, and 0.55 are virtually identical. For $x = 0.83$, corresponding to the fictitious compound Cu_5InS_4, a superposition of the unbroadened $CuInS_2$ signal and a much narrower ($\Delta B = 0.5$ G) symmetrical signal is observed. Spectra were analyzed under the assumption that Eq. (1) is valid for the description of the composition-dependent broadening. The width ΔB_b deduced for the broadening function $g_b(B)$ is shown in Fig. 4. It saturates for $x < 0.45$ and becomes con-

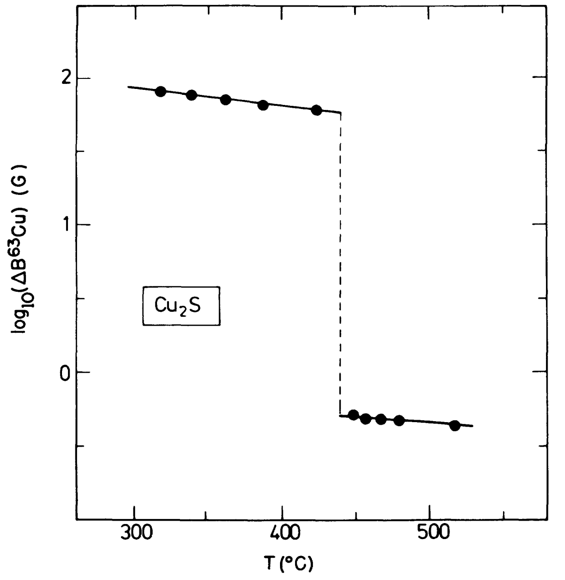

FIG. 5. Linewidth for ^{63}Cu in stoichiometric Cu_2S as a function of temperature; $\nu_L = 16$ MHz.

stant for $x \geq 0.50$.

The temperature dependence of the absorptions for the nonstoichiometric compositions was studied in detail only at $x = 0.48$. Similar to the stoichiometric case the absorption underwent a change characteristic of dipolar motional narrowing of about 350 °C. Above this temperature the line shape was essentially independent of temperature. No notable differences appeared to exist between the samples with $x = 0.50$ (Fig. 1) and $x = 0.55$. On the other hand, for $x = 0.40$ and 0.45, the absorption signals become weaker with increasing temperature and finally disappeared. Thus a temperature-dependent line-broadening mechanism must be operative in this highly Cu_2S-deficient material.

B. ^{63}Cu in Cu_2S

The symmetrical shape of the narrow line observed for $x = 0.83$ at 450 °C indicates the presence of a second phase of cubic or near-cubic structure. It is logical to attribute this signal to Cu_2S which at a temperature between 430 and 450 °C transforms from a hexagonal to a cubic high-temperature phase.[15] Figure 5 shows $\Delta B(^{63}Cu)$ in Cu_2S in the temperature range around this phase transition. To unambiguously set the composition during the measurements, the substance was held at equilibrium with metallic copper. In the noncubic phase, the broad absorption possesses a line shape characteristic of a static quadrupole effect of second order. Above the transition, which was observed by NMR to occur at 440±5 °C, the line is symmetrical and its width agrees with that encountered in "Cu_5InS_4." Our data are in good agreement with results obtained by Schaefgen[16] for a similarly prepared sample. Under the assumption that $\nu(Cu^+) \gg \nu_L = 10^8$ s^{-1}, the temperature dependence of ΔB will be determined by that of the copper ionic motion. For the enthalpy of activation of this motion in cubic Cu_2S, we obtain a value of 0.15 eV, which is significantly smaller than the 0.24 eV derived from ionic conductivity measurements on hexagonal Cu_2S.[15]

Cu_2S itself is the compound in equilibrium with $CuInS_2$ on the Cu_2S-rich side. According to Binsma *et al.*,[17] the spinel-type $CuIn_5S_8$ is the coexistent compound on In_2S_3-rich side. We did no succeed in detecting a copper absorption with the moderate signal averaging employed in our experiments. Therefore we conclude that a $CuIn_5S_8$ line must be very broad.

C. ^{63}Cu in $CuInSe_2$

The line shape shows a temperature dependence[18] (Fig. 6) similar to $CuInS_2$. ΔB_b narrows between 300 and 400 °C again resulting in $\nu(Cu^+) = 3 \times 10^3$ s^{-1} at about 350 °C. However, already at room temperature the spectrum exhibits pronounced asymmetry. Therefore, the $CuInSe_2$ spectra are not amenable to a determination of ΔB_b sufficiently precise for the calculation of an enthalpy of activation. As in the case of $CuInS_2$, material prepared by reaction of either the elements or the binary compounds shows the same behavior.

D. ^{63}Cu in $CuInTe_2$

The temperature dependence of ΔB (Fig. 6) in the sample produced by elemental synthesis (sample *A*) is similar to that in the stoichiometric sulfide and selenide chalcopyrite-structure compounds, shown in Figs. 2 and 6. The slight bend in $\Delta B(T)$ at about 350 °C indicates the onset of motional narrowing of $g_b(B)$. Thus the mobility of the cuprous ions in the three stoichiometric chalcopyrite-structure compounds is similar. However, in $CuInTe_2$ we never observed the pronounced fine structure encountered in $CuInS_2$ and $CuInSe_2$ at high temperatures. The $CuInTe_2$ spectra at best resembled those shown in Fig. 3 for slightly Cu-deficient samples.

Quite a different behavior is exhibited by a sample made from part of a zone-leveled crystal, sample *B* of Fig. 6. Here, the linewidth at room temperature is 2.4 G as compared to 3.0 G for sample *A*. Corre-

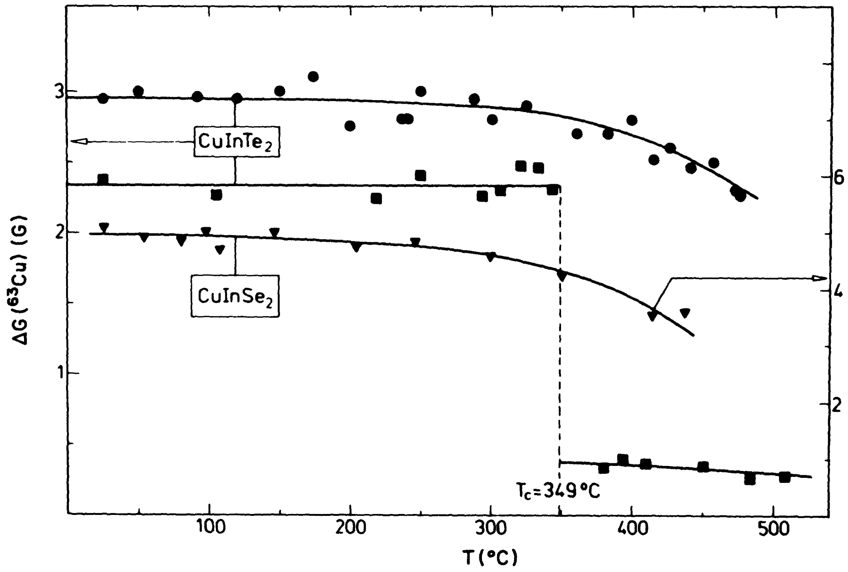

FIG. 6. Total linewidth for $^{63}\mathrm{Cu}$ in $\mathrm{CuInSe_2}$ (▼) and in nominally stoichiometric (●, sample *A*) and nonstoichiometric (■, sample *B*) $\mathrm{CuInTe_2}$; $\nu_L = 16$ MHz.

spondingly, the quadrupole coupling constants differ slightly: 0.57 MHz for sample *A* vs 0.50 MHz for sample *B*. Furthermore, at 350 °C the linewidth of the nearly symmetric absorption in sample *B* drops abruptly from 2.4 to 0.3 G. In the vicinity of this temperature, reproducible spectra were difficult to take because of pronounced sintering of the powered sample. By differential scanning calorimetry (Perkin Elmer DSC 2), a thermal peak was observed in sample *B* at 349±1 °C, associated with an enthalpy change of $\Delta H = 0.30\ \mathrm{kJ\,mol^{-1}}$. Above this temperature the NMR spectrum does not contain any fine structure. One obvious interpretation is that the transition results from a melting of the cation lattice leading to a random distribution of Cu and In in a zinc-blende structure. This explanation must be discarded since high-temperature x-ray diffraction at 400 °C still indicated the ordered Cu-In superstructure. The superstructure lines and the appearance of weak additional lines rather support the suggestion of Zalar[19] that $\mathrm{CuInTe_2}$ may decompose into two or more phases when heated above 350 °C.

No sintering and no thermal effects are observed in sample *A* up to a high-temperature solid-state phase transition which we detected by differential thermal analysis (DTA) in sample *A* and *B* at 665 °C (Table I). This temperature is in reasonable agreement with the transition reported by Zalar "near 650 °C."[19] In summary, we attribute the line narrowing at 350 °C encountered in sample *B* to deviations from exact stoichiometry in the piece of the zone-leveled crystal investigated.

E. $^{115}\mathrm{In}$ in $\mathrm{CuInS_2}$, $\mathrm{CuInSe_2}$, $\mathrm{CuInTe_2}$

While the absorptions of $^{63}\mathrm{Cu}$ reflect ionic motion in the chalcopyrites, the $^{115}\mathrm{In}$ NMR spectra are determined by static quadrupole effects. $\Delta B(^{115}\mathrm{In})$ as a function of temperature for $\mathrm{CuInS_2}$ and

TABLE I. Phase transformation temperatures in degrees centigrade measured by differential thermal analysis.

Compound	T_1	T_2	T_m
$\mathrm{CuInS_2}$	975[a]	1045[a]	1095[a]
	980[b]	1045[b]	1090[b]
			1000–1050[c]
$\mathrm{CuInSe_2}$	665[a]	810[a]	987[a]
			990[c]
$\mathrm{CuInTe_2}$	349[a,d]	665[a,e]	785[a,e]
		~650[f]	780[f]

[a] This study.
[b] Reference 17.
[c] From Ref. 1.
[d] Nonstoichiometric $\mathrm{CuInTe_2}$ sample *A*.
[e] Identical for sample *A* and *B* within experimental accuracy of ±2 °C.
[f] Reference 19.

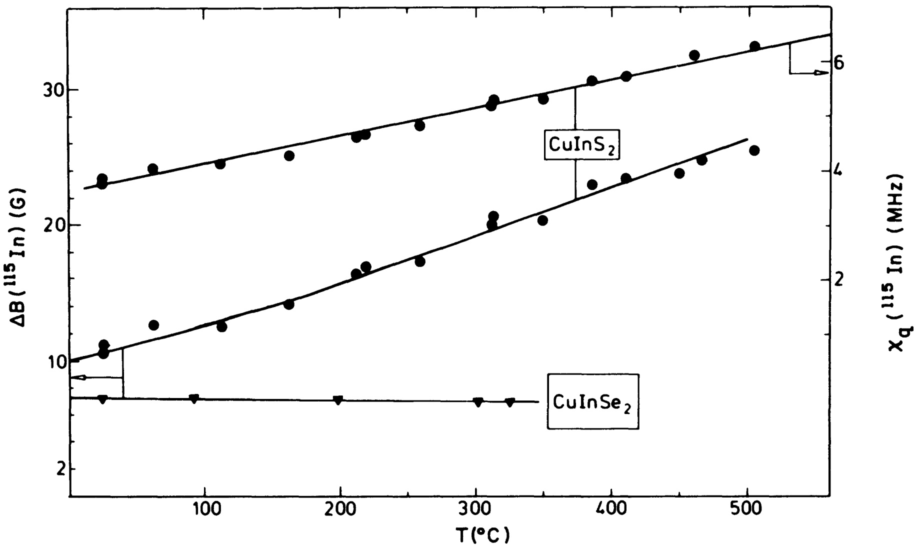

FIG. 7. Total linewidth for ^{115}In in $CuInS_2$ (●) and $CuInSe_2$ (▼), $\nu_L = 13$ MHz, and quadrupole coupling constant of ^{115}In in $CuInS_2$.

$CuInSe_2$ is shown in Fig. 7. For $CuInTe_2$, we measure a width at room temperature of 82 G ($\nu_L = 11.8$ MHz). We did not investigate the temperature dependence of this signal. Also shown in Fig. 7 is the quadrupole coupling constant in $CuInS_2$ which increases linearly with temperature: $|\chi_q| = 2.2 + 5.2 \times 10^{-3} T$ (MHz). In $CuInSe_2$, ΔB and hence χ_q show no temperature dependence.

F. Phase-transformation temperatures

The possible existence of high-temperature modifications with cubic structure led us to study the $CuInX_2$ compounds by differential thermal analysis. The phase-transition temperatures are shown in Table I. They are in reasonable agreement with the temperatures of transitions detected in earlier work. As far as we know, the transition in $CuInSe_2$ at $T_1 = 665$ °C has not been reported earlier.

III. DISCUSSION

The quadrupole coupling constants obtained in our study are listed in Table II. We obtained a $|\chi_q(^{63}Cu)|$ for $CuInS_2$ of 0.54 MHz. This value is in agreement with the upper limit of 1.1 MHz derived by Spiess *et al.*,[3] but not with the measurement of Peterson[2] (5.41 MHz) or the calculations of Lines[5] (5.38 MHz). We observed identical χ_q on samples from different sources and produced by different methods. Therefore we see no way to recon-

TABLE II. Quadrupole coupling constants $|\chi_q|$ of ^{63}Cu, ^{27}Al, ^{69}Ga, and ^{115}In for $CuZX_2$ compounds at room temperature in MHz. The lattice parameter ratios c/a indicate the degree of tetragonal distortion.

Compound	$\|\chi_q(^{63}Cu)\|$	$\|\chi_q(III)\|$	c/a
$CuAlS_2$	5.60[a]	0.867[a]	1.958[a]
	5.97[b]		
$CuAlSe_2$	5.16[a]		1.954[a]
$CuAlTe_2$	2.95[c]		1.97_5[d]
$CuGaS_2$	5.46[a]	1.80[a]	1.948[a]
	5.61[b]		
$CuGaSe_2$	4.64[a]	<1[a]	1.965[a]
	4.64[b]		
$CuGaTe_2$	2.64[b]		1.98_7[d]
$CuInS_2$	<1.1[a]	<5[a]	2.013[a]
	0.54[c]	3.8[c]	
$CuInSe_2$	<1.4[a]	<5[a]	2.008[a]
	0.75[c]	2.9[c]	
$CuInTe_2$	0.57[c]	11.0[c]	2.008[e]
$CuTlS_2$	0.57[c]		2.019[f]
$CuTlSe_2$	0.54[c]		1.99_5[d]
$CuFeS_2$	4.1[h]		1.96_5[g]

[a] Reference 3.
[b] Reference 2.
[c] This study.
[d] Reference 20.
[e] Reference 19.
[f] Reference 21.
[g] Reference 22.
[h] Deduced from the data reported in Ref. 23.

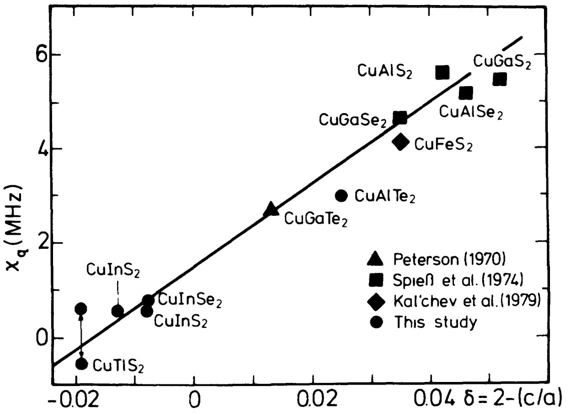

FIG. 8. Quadrupole coupling constant of ^{63}Cu in copper-containing chalcopyrite-structure compounds as a function of the tetragonal distortion parameter, $\delta = 2 - c/a$.

cile this discrepancy, which clearly is of concern. The $|\chi_q(^{63}\mathrm{Cu})|$ values for CuTlS$_2$ disagree to a similar extent (Table II).

To complement earlier interpretations of χ_q in terms of localized bonding,[2,3,5] we also determined the coupling constants of ^{63}Cu in CuAlTe$_2$, CuTlS$_2$, and CuTlSe$_2$ and analyzed the quadrupole interaction in the copper-containing *IB*-III-VI$_2$ chalcopyrite-structure compounds as a function of the tetragonal distortion parameter $\delta = 2 - c/a$. The result is shown in Fig. 8. CuTlSe$_2$ is not included due to the lack of precise lattice parameter data. The linear correlation is striking. The dependence of $|\chi_q(^{63}\mathrm{Cu})|$ on δ is well described by $|\chi_q| = 1.50 + 90\delta$ MHz. The ambiguity in the sign of the coupling constant prevents a unique interpretation of the temperature dependence of ΔB_q in CuInS$_2$ as a function of tetragonal distortion. In the following paragraph we argue that χ_q is positive for all copper-containing chalcopyrite-structure compounds with the possible exception of CuTlS$_2$. If this is the case, the correlation between $|\chi_q|$ and δ will also apply to χ_q.

For the undistorted ideal structure, $|\chi_q(\delta=0)|\,1.5 \pm 0.2$ MHz. This value is of the same order of magnitude as the result of a point-charge model accounting for the contribution of only the lattice charges to the electric field gradient $eq = V_{zz}$, such that $V_{zz} = (1-\gamma_\infty)V_{zz}^{\mathrm{lat}}$.[11] $1-\gamma_\infty$ is the Sternheimer shielding factor. Under this condition, the then exact tetrahedral symmetry of the electronic charge distribution on the noble metal ions causes the orbital contribution to V_{zz} to vanish. We calculated the EFG acting on the group-*IB* metal sites by summation over 30 000 metal ligands

$$V_{zz}^{\mathrm{lat}} = 3.15(z_{\mathrm{I}}^{*} - z_{\mathrm{III}}^{*})ea^{-3}\,, \qquad (5)$$

where $a = c/2$ is the quasicubic lattice parameter. To allow for partial covalency, $z_{\mathrm{I}}^{*} - z_{\mathrm{III}}^{*} = -1.7$ (Ref. 5) was used as an estimate for the average difference in the effective charges on the metal ions. The Sternheimer shielding factor $(1-\gamma_\infty)$ was taken to be 26.2 for Cu^{+} crystal ions[24] and Q as -0.209×10^{-24} cm^2 (Ref. 25). For the range of lattice constants covered by the chalcopyrite-structure compounds, we calculate $4.3 \le \chi_q \le 6.8$ MHz. The agreement, within an order of magnitude of $|\chi_q(\delta=0)|$, is not unreasonable in view of the simple point-charge model in which higher moments in the charge distribution of the lattice are neglected. We assume, in the spirit of this discussion, that χ_q is positive for all compounds with the possible exception of CuTlS$_2$ (Fig. 8). If we now attribute the temperature dependence to thermal changes of the lattice parameters, the decrease of $|\chi_q|$ with rising temperature for the case of CuInS$_2$ (Fig. 2) may be taken as an indication of increasing tetragonal distortion $(d\delta/dT < 0)$: The unit cell elongates. However, the x-ray data of Binsma *et al.*[17] show that CuInSe$_2$ approaches $c/a = 2.00(\delta = 0)$ with increasing temperature, a result confirmed by our own high-temperature x-ray diffraction study. Therefore we associate the temperature dependence of ΔB_q with dynamic effects. The diffusing Cu(I) ions sample EFG's, which decrease slightly with temperature.

Apart from these static quadrupole effects, the main result of our study is the detection of motional narrowing for ^{63}Cu in all three stoichiometric compounds. For CuInS$_2$ we are able to deduce a copper-diffusion coefficient as well as its enthalpy of activation. Our data show that the diffusion of Cu^{+} is not particularly rapid. This finding is at variance with expectations based on the fact that a number of cuprous compounds with fcc anion lattices exhibit fast ionic conduction. The cubic high-temperature phases of the binary chalcogenide-structure compounds such as Cu$_2$S and CuI represent such examples with average jump frequencies of Cu^{+} and CuI of the order of 10^{9}–10^{10} s^{-1} at 370 °C.[28] In CuInS$_2$ at the same temperature, $\nu(\mathrm{Cu}^{+})$ is 3×10^{3} s^{-1}. One reason for the much slower diffusion in CuInX_2 certainly is the presence of the highly charged group-III atoms and their ability to stabilize the ordered superstructure even up to high temperatures. A similar observation has been made for Cu(I) cations in sulvanite-structure Cu$_3$VX_4.[18] Disordered cubic chalcopyrite phases with high cation mobilities may prove interesting for comparison with copper(I) and silver chalcogenide-structure compounds.

The absence of extensive line narrowing in the copper-deficient samples demonstrates that the ^{63}Cu resonance is sensitive to deviations from the ideal composition. Our observation may indicate either a much slower rate of Cu diffusion, or an offsetting quadrupolar contribution to the broadening function $g_b(B)$. For the stoichiometric case we did not consider such a contribution which, however, may become significant in the presence of large concentrations of lattice defects. In the slightly Cu-deficient sample with $x = 0.48$, we observed dipolar motional narrowing at about the same temperature as in the stoichiometric sample. The quadrupole line shape was virtually independent of temperature up to 550 °C. This observation confirms unequivocally that a quadrupolar contribution keeps $\Delta B(T)$ from decreasing.

For the system $(Cu_2S)_x(In_2S_3)_{1-x}$ NMR provides information about the region of existence of $CuInS_2$. The additional quadrupolar contribution to $g_b(B)$ tracks the incorporation of excess In_2S_3 in the crystal. This interpretation is also consistent with the fact that the overall width of the signal is influenced only very little by the deviation from the exact composition. It is mainly the reduction of signal intensity which, apart from the line shape, reflects the changes in the broadening function for $x < 0.50$. Such reductions in intensity occur if the width of $g_b(B)$ is comparable to or larger than ΔB_q. For $x > 0.50$, no additional quadrupolar interactions arise. This can easily be understood if the homogeneity region of $CuInS_2$ does not extend to the Cu-rich side. Then, as we have shown for $x = 0.83$, excess Cu_2S precipitates as a second phase. These conclusions agree with the results of an x-ray investigation of the phase diagram of $CuInS_2$ (Ref. 17): In quenched samples, a region of existence of $0.48 \leq x \leq 0.50$ was determined at room temperature. Our result, obtained at 450 °C (Fig. 4), is $0.45 \leq x \leq 0.50$. Thus we have demonstrated the use of NMR as a sensitive method with high resolution for the investigation of existence ranges of solid phases.

Finally, we should like to comment on the temperature-dependent intensity loss observed in the sample with $x = 0.40$ and 0.45. This loss may have two very different origins. If the excess In_2S_3 is not completely incorporated into the crystal at low temperatures, the intensity loss may be caused by dissolution of In_2S_3 in $CuInS_2$ with increasing temperature. This heterogeneous type of broadening is discussed above and is essentially of static nature. On the other hand, motion of lattice defects, whose concentrations must be large in these off-stoichiometric substances, can cause lifetime broadening of quadrupole-sensitive nuclear absorptions.[27] For this phenomenon to occur the average frequency of EFG fluctuations associated with the defect motion must reach the order of magnitude of the Larmor frequency of the NMR experiment, i.e., 10^8 s^{-1}. In this case, NMR provides also a means to investigate the diffusion of lattice defects prevailing in nonstoichiometric chalcopyrite-structure compounds.

For nominally stoichiometric $CuInSe_2$ and $CuInTe_2$ we did obtain a diffusion coefficient for Cu^+, but the linewidth data do not allow for the determination of its temperature dependence. In contrast to $CuInSe_2$, no drastic narrowing of the broadening function $g_b(B)$ was observed for $CuInTe_2$. In light of the results obtained in the Cu_2S-In_2S_3 system, the absence of extreme narrowing strongly suggests that $CuInTe_2$ does not exist as a stoichiometric compound. This conclusion is in agreement with the results obtained by Palatnik and Rogacheva[7] in their investigation of the $(Cu_2Te)_x(In_2Te_3)_{1-x}$ phase diagram. According to these authors, up to the highest temperatues, $CuInTe_2$ in equilibrium with Cu_2Te contains an excess of In_2Te_3 with $x \cong 0.48$. Such a deviation from exact stoichiometry provides an independent confirmation of the high-temperature line shape observed for $^{63}CuInTe_2$.

Owing to the very abrupt line narrowing for ^{63}Cu at 350 °C in off-stoichiometric $CuInTe_2$ (sample B), we could not evaluate a diffusion coefficient. We attribute the line narrowing to a phase change resulting in the formation of a small amount of a secondary phase, probably InTe. Segregation of Cu_2Te, similar to that discussed for the Cu_2S-In_2S_3 system for $x = 0.83$, can be excluded since $\Delta B(^{63}Cu_2Te) \sim 4$ G at this temperature.[16] These phenomena may be related to the "conductivity pockets" observed by Zalar in his work on nonstoichiometric $CuInTe_2$.[19] The absence of quadrupolar fine structure above the transition temperature requires the operation of fast diffusion between the crystallites of the powdered sample, with $D(Cu^+) \gg 10^{-12}$ cm^{2}s^{-1}. A high rate of copper diffusion in the bulk of the material may be facilitated by a large concentration of lattice defects formed in the decomposition when heating above 350 °C. This explanation for the absence of quadrupolar fine structure is also supported by the observation of extensive sintering of the initially powdered material. Also in line with this interpretation of the phase behavior of $CuInTe_2$ is the magnitude of the entropy change which appears to be too small to correspond to an order-disorder phase transition in the solid state. The estimated entropy change for this transition is 3.9 J K^{-1} mol^{-1}.[17]

IV. SUMMARY

In this study we demonstrated the application of high-temperature NMR to kinetic, thermodynamic, and structural aspects of the three quasicubic compound semiconductors CuInX_2 ($X \equiv$S,Se,Te) and of Cu_2S. We deconvoluted the absorption signals of ^{63}Cu and ^{115}In into the magnetic dipole and the nuclear quadrupole contributions whenever possible. The most detailed data were obtained for $CuInS_2$, where we measured the NMR spectra not only as a function of temperature but also as a function of composition. For all compounds of exactly stoichiometric composition we observed motional narrowing of the ^{63}Cu signal and calculated Cu^+ jump frequencies. The composition of chalopyrite-structure $CuInS_2$ at 450 °C ranges from $Cu_{1.00}In_{1.00}S_2$ to $Cu_{0.85}In_{1.05}S_2$. For copper content higher than this range the $^{63}CuInS_2$ signal reflected the contribution of ^{63}CuS. We determined by NMR the hexagonal → cubic transition of Cu_2S at 440 °C, and an activation energy of 0.15 eV for the Cu^+ jump frequency in the cubic modification. In the course of a check of the phase transformation temperatures in the three CuInX_2 compounds, we detected a phase transition of $CuInSe_2$ at 665 °C which previously had gone unnoticed. For the quadrupole coupling constant χ_q of a group of CuZX_2 compounds we discovered a linear correlation with the tetragonal distortion parameter. At $\delta = 0$, the $|\chi_q|$ of 1.50 MHz is comparable to the result of a calculation in which the electric field gradient is set up by point charges on a cubic lattice.

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