Phonons in Cu_3Au near the Order-Disorder Transition

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(Received 19 June 1989)

Selected phonon modes in Cu_3Au have been studied at temperatures in the vicinity of the order-disorder transition by neutron-scattering techniques. Marked changes occur predominantly at temperatures well below the region of the precipitous drop in the order parameter. Our results give considerable support to the concept of spinodal ordering near a discontinuous phase transition, and are consistent with a lower spinodal temperature of $T_c - 24$ K as inferred from earlier x-ray-scattering results.

PACS numbers: 63.20.Dj, 63.50.+x, 64.60.Fr

The order-disorder phase transition which occurs in Cu_3Au has been extensively studied and is considered a prototype for discontinuous or first-order phase transitions. The underlying lattice on which the Cu and Au atoms reside is a face-centered-cubic lattice. In the high-temperature disordered phase, Cu and Au atoms are randomly distributed on the lattice sites. In the low-temperature ordered phase, Au atoms preferentially occupy the cube-corner positions within the unit cell while Cu atoms preferentially occupy the face-centered positions, leading to the formation of a superlattice.

There has recently been a resurgence of interest in Cu_3Au. Time-resolved x-ray-scattering studies[1-3] have investigated the kinetics of the ordering process in samples rapidly quenched through the phase transition. Elastic-neutron-scattering measurements[4] of the thermal motion of the atoms have been carried out near the phase transition and neutron-inelastic-scattering measurements[5] have been carried out in the low-temperature ordered phase. The elastic-neutron-scattering measurements[4] and previous x-ray measurements[6] of the temperature dependence of the superlattice Bragg-peak intensity have shown that marked changes in the intensity (which is proportional to the square of the order parameter) occur only within ~4 K of the phase transition. There were also earlier neutron-inelastic-scattering measurements[7] on Cu_3Au in both the ordered and disordered phases as well as neutron-inelastic-scattering and diffuse-x-ray-scattering measurements[8] near the phase transition.

The motivation for much of this work has been the tantalizing possibility of observing effects related to an expected spinodal transition. In the context of the Landau theory of phase transitions, a spinodal transition[9,10] can occur in a system undergoing a discontinuous phase transition and the lower spinodal point, T_s, denotes the temperature at which, on warming from low temperatures, a subsidiary minimum in the free energy as a function of order parameter first appears. Metastable droplets of the disordered phase can then fluctuate out of the ordered phase for temperatures between T_s and the actual first-order transition temperature T_c. The concept of the spinodal transition provides two additional temperature scales for ordering (corresponding to the lower and upper spinodal points) which are not present for a system undergoing a continuous phase transition.

The neutron-scattering results of Chen, Cohen, and Ghosh[8] for phonons at low-symmetry positions in the Brillouin zone and for a restricted range of temperatures near T_c showed only marginal effects in the phonon linewidths. However, their diffuse-x-ray-scattering measurements around the superlattice position gave an extrapolated divergence in the intensity at $\sim T_c - 24$ K and this was interpreted as evidence for a spinodal transition below the first-order phase transition. A recent time-resolved x-ray-scattering study[3] of the kinetics of domain growth has, however, indicated that the early-time kinetic behavior of Cu_3Au is not adequately described by classical spinodal theory.

In the hope of casting further light on the intriguing problem of spinodal transitions, we have carried out new neutron-inelastic-scattering measurements on Cu_3Au with particular emphasis on phonons at selected high-symmetry points in the Brillouin zone. These measurements were made on an initially ordered sample at temperatures from well below to somewhat above the order-disorder transition. The phonon spectra are of course expected to be markedly different in the ordered and disordered phases since the system must change over from having four atoms per unit cell in the low-temperature phase to having one atom per unit cell in the high-temperature phase. In an "effective medium" picture (where one averages over force constant and mass disorder), the disordered phase should exhibit only acoustic-phonon modes across the Brillouin zone. The ordered phase will, however, display both optic and acoustic modes across its (simple-cubic) zone. Most interestingly, our results show that, on raising the temperature, pronounced changes in the phonons occur predominantly at temperatures *well below* the region in which the order parameter drops precipitously to zero at the first-order phase transition. Our results for zone-center modes are consistent with a lower spinodal transition temperature ~24 K below T_c, as inferred from the diffuse-x-ray-scattering study.[8] The zone-boundary modes, however, continue to evolve as the temperature is raised through T_c, indicating that the spinodal transition has a less dramatic effect here than at the ordered-phase zone center (i.e., the ordering wave vector), as one might have anticipated.

The experiment was performed on the N5 triple-axis spectrometer at the NRU reactor of Chalk River Nuclear Laboratories. The single-crystal sample of Cu_3Au was cylindrical in shape with a diameter of 1.3 cm and a length of 9 cm. It was mounted in a vacuum furnace with the (h,h,l) plane of the sample in the scattering plane of the spectrometer. The sample temperature was controlled to better than ±0.5 K. The spectrometer was operated in the constant-**Q** mode ($\hbar\mathbf{Q}$ is the momentum transfer) with a fixed scattered-neutron frequency of 5 THz for inelastic scans and 7 THz for elastic scans. Ge(113) and Si(111) reflections were employed as monochromator and analyzer, respectively. Both of these reflections have systematic absences for second-order neutrons (wavelength $\lambda/2$). A sapphire filter, cooled to 77 K, was inserted in the white beam before the monochromator to further reduce higher-order contamination. The collimations between monochromator and sample, sample and analyzer, and analyzer and detector were 0.54°, 0.59°, and 2.6°, respectively.

Elastic and inelastic scans were performed at seven temperatures from 280 to 692 K. Following each temperature change, the lattice parameter and superlattice Bragg-peak line shape were monitored in order to insure that the sample was in equilibrium prior to commencing data collection. The elastic scattering intensity can be written as[11]

$$S(\mathbf{Q}) \sim \sum_l \exp(i\mathbf{Q}\cdot\mathbf{r}_l) \left| \sum_j b_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j) \right|^2,$$

where the sum over l is over all the unit cells in the system and the sum over j is over the atoms having scattering lengths b_j and positions $\mathbf{r}_j$ within each unit cell. The Debye-Waller factor has been ignored in this expression. Consequently, the order parameter is proportional to the square root of the superlattice Bragg-peak intensity. We have measured the intensity at the (0,0,3) superlattice point. The results (see Fig. 1) give a first-order transition temperature, T_c, of 657±3 K for our Cu_3Au sample. While there is a gentle decrease in intensity as the transition is approached from below, dramatic changes in the elastic scattering are restricted to temperatures within about 4 K of T_c. This is consistent with previous measurements[4,6] of the elastic scattering from Cu_3Au.

The elastic scattering is only sensitive to the scattering-length disorder parallel to the wave-vector transfer **Q**. The inelastic scattering, on the other hand, is sensitive to force-constant disorder, mass disorder, and scattering-length disorder. Therefore, the phonon spectra would be expected to be considerably more sensitive to the presence of disorder than is the elastic scattering. Quite generally one can write the inelastic neutron scattering as[11]

$$S(\mathbf{Q},\omega) = \langle n(\omega)+1 \rangle \mathrm{Im}\chi(\mathbf{Q},\omega),$$

where $\hbar\omega$ is the energy transfer, $\langle n(\omega)+1\rangle = [1 - \exp(-\hbar\omega/k_B T)]^{-1}$ is the thermal population factor, and $\mathrm{Im}\chi(\mathbf{Q},\omega)$ is the imaginary part of the dynamic susceptibility, which contains the physics of the system under study. It is thus straightforward to divide the measured $S(\mathbf{Q},\omega)$ by the exactly known quantity $\langle n(\omega)+1\rangle$ to obtain $\mathrm{Im}\chi(\mathbf{Q},\omega)$, and this is what we shall do. It should be noted that the elastic neutron scattering measures the quantity $S(\mathbf{Q},\omega=0)$, while the x-ray-diffraction measurements integrate over all frequencies relevant to Cu_3Au and, in fact, measure $\int S(\mathbf{Q},\omega) d\omega$.

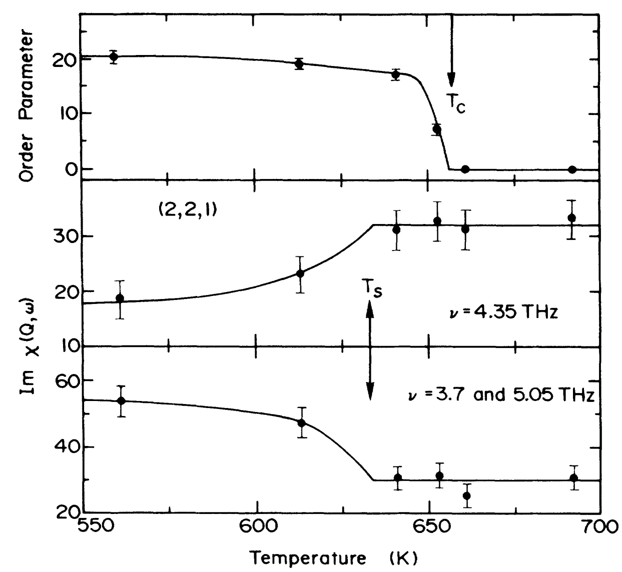

FIG. 1. Top panel: The temperature dependence of the order parameter, as deduced from the square root of the (0,0,3) superlattice intensity. Bottom panels: $\mathrm{Im}\chi(\mathbf{Q},\omega)$ for the (2,2,1) scan at selected frequencies (see Fig. 2). All curves shown are guides to the eye. The value of T_s shown by the arrow indicates the temperature ($T_c - 24$ K) of the extrapolated divergence of diffuse-x-ray-scattering intensity (Ref. 8).

The **Q** values chosen for this study were points of high, but different, symmetry in the low- and high-temperature phases. Specifically, they were the Γ points (2,2,1) and (0,0,3), and X points (2,2, −0.5) and (0,0,3.5). The Γ points are zone centers in the ordered phase and zone boundaries in the disordered phase, while the X points are zone boundaries in the ordered phase and half way to the zone boundary in the disordered phase. Since we were unable to obtain results of high quality at (0,0,3) and (0,0,3.5) in the time available, we shall, in this Letter, restrict our attention to the results at (2,2,1) and (2,2, −0.5). Typical results for $\mathrm{Im}\chi(\mathbf{Q},\omega)$ at (2,2,1) are shown in Fig. 2. At this wave vector, in the low-temperature ordered phase, two optic phonons having flat dispersion (ω independent of **Q**) are observed. Because of the flat dispersion, the **Q** resolution and the frequency resolution are decoupled. The full width at half maximum of the frequency resolution was ~0.35 THz.

At $T=561$ K (as at lower temperatures) there are two well-defined phonon peaks, at ~3.75 and ~4.95 THz. These peaks broaden and merge as the temperature is raised, with most of the change occurring between 613 (T_c-44 K) and 641 K (T_c-16 K). By 641 K, $\mathrm{Im}\chi(\mathbf{Q},\omega)$ has largely assumed the form characteristic of the high-temperature disordered state, as is most clearly shown by the bottom panel of Fig. 2 where we have plotted $\mathrm{Im}\chi(\omega,T=692\ \mathrm{K})-\mathrm{Im}\chi(\omega,T=641\ \mathrm{K})$ for this wave vector. It is interesting to note that the width of the phonon peak observed in the disordered state is surprisingly large (~3 times our experimental resolution). This suggests that a spinodal transition may still be playing a role at 692 K and that additional measurements at even higher temperatures might be valuable.

To summarize our results for (2,2,1) more completely, we have plotted, in the bottom panel of Fig. 1, $\mathrm{Im}\chi(\mathbf{Q},\omega)$ for three frequencies and for all temperatures studied in the range 561–692 K. The frequencies are approximately those of the two phonon peaks and the minimum between them at 561 K. The values of $\mathrm{Im}\chi(\mathbf{Q},\omega)$ shown in Fig. 1 represent the sum at four or five measured frequencies around the stated ν values ($\nu=\omega/2\pi$). The qualitative behavior of $\mathrm{Im}\chi(\mathbf{Q},\omega)$ at the two-phonon peak frequencies is the same, and we have added the data at these two frequencies together for the plot in Fig. 1. Here we can see very clearly that the changes in the phonon modes for (2,2,1) are essentially complete at a temperature well below the region in which the sudden drop in the order parameter (top panel of Fig. 1) occurs. There is certainly no significant change above 641 K (T_c-16 K) and the curves suggest that the changes are probably complete by about 630 K (T_c-27 K). These curves are primarily meant to be guides to the eye. The point of inflection is not very accurately determined by our measurements but there is clear consistency between the temperature at which the changes in the phonon spectra are complete and the temperature (~T_c-24 K) of the extrapolated divergence in the diffuse-x-ray-scattering intensity[8] mentioned earlier. We identify the temperature at which we observe this change in dynamical behavior in Cu_3Au as the lower spinodal temperature, T_s. Very interestingly, a thorough study[12] of phonons in CuZn, a system whose transition is

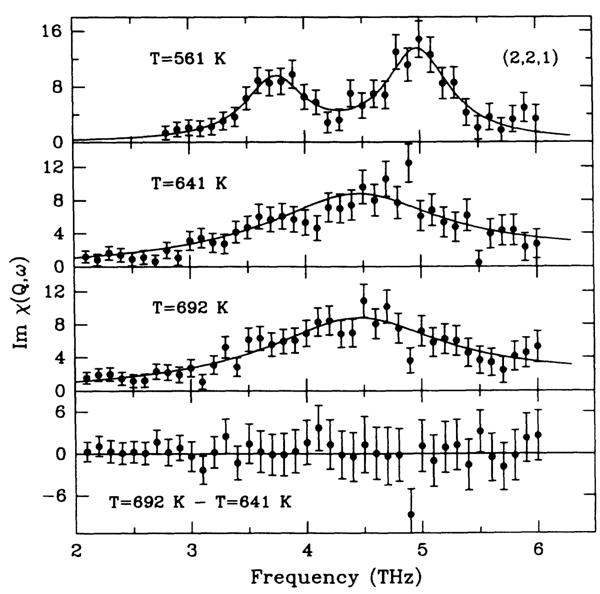

FIG. 2. $\mathrm{Im}\chi(\mathbf{Q},\omega)$ (in arbitrary units) at the Γ point (2,2,1) for temperatures of 561, 641, and 692 K. The bottom panel shows the difference between the 692-K data set and the 641-K data set. The curves are guides to the eye.

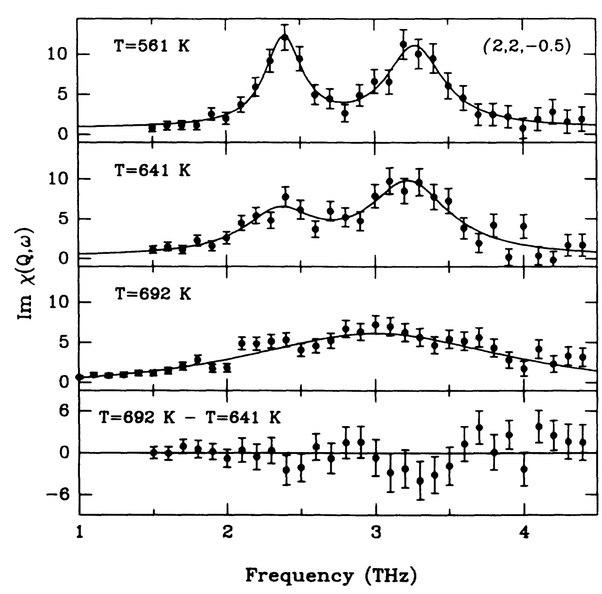

FIG. 3. $\mathrm{Im}\chi(\mathbf{Q},\omega)$ (in arbitrary units) at the X point (2,2, −0.5) for temperatures of 561, 641, and 692 K. The bottom panel shows the difference between the 692-K data set and the 641-K data set. The curves are guides to the eye.

continuous and therefore without a spinodal, did not reveal any such anomalous behavior.

Our results for $\mathrm{Im}\chi(\mathbf{Q},\omega)$ at the X wave vector, $(2,2,-0.5)$, are shown in Fig. 3. The solid curves are simply guides to the eye. At 561 K, as at lower temperatures, we observe two well-defined peaks corresponding to an acoustic mode at ~ 2.4 THz and an optic mode at ~ 3.28 THz. As at (2,2,1), the peaks broaden and merge as the temperature is raised, eventually producing an apparently single broad peak at 692 K. While substantial changes in $\mathrm{Im}\chi(\mathbf{Q},\omega)$ have occurred by 641 K, further changes continue above this temperature in contrast to the results for the Γ wave vector, (2,2,1). This is clearly seen in the bottom panel of Fig. 3 which shows $\mathrm{Im}\chi(\omega,T=692\text{ K})-\mathrm{Im}\chi(\omega,T=641\text{ K})$. The two phonon modes at $(2,2,-0.5)$ appear to evolve differently with temperature. The lower-energy acoustic mode has undergone a dramatic change from its low-temperature form by 641 K, while the higher-energy optic mode has changed relatively little by 641 K but then changes markedly on passing through the transition at 657 ± 3 K. Our data thus show that the spinodal effects are more marked and complete at the ordering wave vector (the ordered-phase zone center) than at the zone boundary. While our results give considerable support to the concept of a spinodal transition below T_c, a more sophisticated theoretical approach is needed to provide a quantitative understanding of all of our data.

To summarize, we have performed an inelastic-neutron-scattering study of high-symmetry phonons in Cu_3Au for temperatures in the vicinity of the order-disorder transition. Our results have been presented in terms of the imaginary part of the dynamic susceptibility, the quantity which reflects the physics of the system. This model-independent approach has demonstrated that the phonon response, especially at the ordering wave vector, is extremely sensitive to temperature in a temperature region substantially below the discontinuous phase transition, i.e., in a region where the order parameter (as determined by the elastic Bragg scattering) still has close to its full value. This presumably reflects a rapid change in the "disorder" present in the crystal in the temperature region just below T_c-24 K as would be consistent with a spinodal transition occurring in this region. We hope that this study will help to stimulate and guide the more sophisticated theoretical developments that are clearly needed for an adequate quantitative understanding.

This work has benefitted from discussions with M. Hagen, R. M. Nicklow, and M. Sutton. Two of us (B.D.G. and E.D.H.) gratefully acknowledge the hospitality of Chalk River Nuclear Laboratories. This research was supported in part by the U.S. Department of Energy under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., by the Natural Sciences and Engineering Research Council of Canada, and by the Ontario Centre for Materials Research.

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