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Effect of heat treatment on acoustic properties of chromium polycrystals at low temperatures

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Abstract. Acoustic properties of polycrystalline Cr samples of 99.99 % purity are investigated at frequencies of longitudinal vibrations $f \sim 75$ kHz and of bending vibrations at $0.6 < f < 1.5$ kHz when thermocycling within the temperature interval 5 – 330 K. Special attention is paid to the acoustic anomalies in the vicinity of the magnetic phase transitions: the Néel point and the spin-flip transition. In the as-received samples, a significant hysteresis of the acoustic properties has been found for the first time. The effect of heat treatments on internal friction and elastic properties of chromium polycrystals is also investigated. The data obtained are compared with the effect of small preliminary deformation and a long-time ageing at room temperature on the ultrasound anomalies in Cr single crystal. The observed behavior of the acoustic properties may be caused by changes in the antiferromagnetic domain structure in Cr polycrystals under the action of thermoelastic stresses arising from quenching, preliminary plastic deformation or thermocycling.

Introduction

At low temperatures in chromium with the electronic configuration $3d^5 4s^1$, two magnetic phase transitions are observed [1], which are accompanied by structural transformations of the first order. At the Néel point $T_N \approx 309$ K, the paramagnetic-to-antiferromagnetic (PM to AFM) transition takes place with the formation of the transversal spin density wave (TSDW). The paramagnetic chromium has the bcc lattice that below T_N turns into the orthorhombic one at cooling. At the temperature of the spin-flip transition, $T_{SF} \approx 124$ K, the transversal polarization of the spin density waves changes to the longitudinal polarization (LSDW), and the chromium lattice transforms into the tetragonal modification. Earlier, the temperature dependences of the decrement $\delta(T)$ and the dynamic Young's modulus $E(T)$ in Cr single crystals were investigated at the vibration frequencies of $f \sim 89$ kHz, and new acoustic effects were revealed in the vicinity of the magnetic phase transitions [2 – 4]. Along with the known and expected anomalies connected directly with the phase transitions, a strong amplitude dependence was revealed for the first time in the temperature interval $T_{SF} \le T \le T_N$. It was also established that preliminary plastic deformation leads to smearing and splitting of the acoustic anomalies (i.e. in the dependences $\delta(T)$ and $E(T)$) near T_N and also to a displacement of the average value of T_N towards higher temperatures. Ageing of the samples at room temperature for a long time led to a partial recovery of the parameters of the anomalies mentioned.

Some important aspects of elastic and anelastic behavior of chromium crystals at low temperatures appeared, which were beyond the goals of the works [2 – 4]. In particular, no investigations have been made to determine the influence of thermal treatments on the internal friction and the elastic moduli of chromium in the vicinity of the magnetic phase transitions. In addition, all the measurements were made on Cr single crystals. Therefore, possible grain boundary effects have not been studied. In this work, we have investigated the elastic and inelastic properties

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of as-received and annealed polycrystalline Cr samples to establish whether there was an influence of the crystal microstructure on the parameters of the magnetic phase transitions. The measurements were carried out in a wide range of vibration frequencies when thermocycling the samples in the temperature interval from 340 K down to liquid helium temperatures. The results obtained are discussed together with the earlier ones obtained with the single crystals.

Experimental

The acoustic properties of as-received polycrystalline Cr samples of 99.99 % purity with 0.01 % (C+N) content were investigated at frequencies of the forced longitudinal vibrations $f \sim 75$ kHz (the two-component composite vibrator technique [5]) and of the forced bending vibrations [6] at frequencies $0.6 < f < 1.5$ kHz when thermocycling within a temperature interval 330 – 5 – 330 K. The Young's modulus E was determined from the sample resonant frequency f taking into account the temperature changes of the sample length and density. At high frequencies, the measurements were made in the amplitude independent region and the strain amplitude was $\varepsilon_0 \approx 8{\cdot}10^{-8}$. At low frequencies, the strain amplitude was two order of magnitude higher $\varepsilon_0 \approx 1{\times}10^{-5}$ and in some cases corresponded to the amplitude dependent regions of the $\delta(\varepsilon_0)$ and $E(\varepsilon_0)$ dependences.

The temperatures were measured with an absolute accuracy of ± 0.2 K using copper-constantan or Ni-NiCr (Thermocoax LKI 05/50) thermocouples in the temperature range $T > 30$ K and with an absolute accuracy ± 0.05 K using GaAs thermoresistor at temperatures below 30 K. The temperatures were stabilized with a relative accuracy better than $\pm 10^{-4}$ over the entire temperature range by means of the electronic control device. Thermocycling was carried out at heating-cooling rates varying from 0.1 to 2 K/min depending on the measurement temperature.

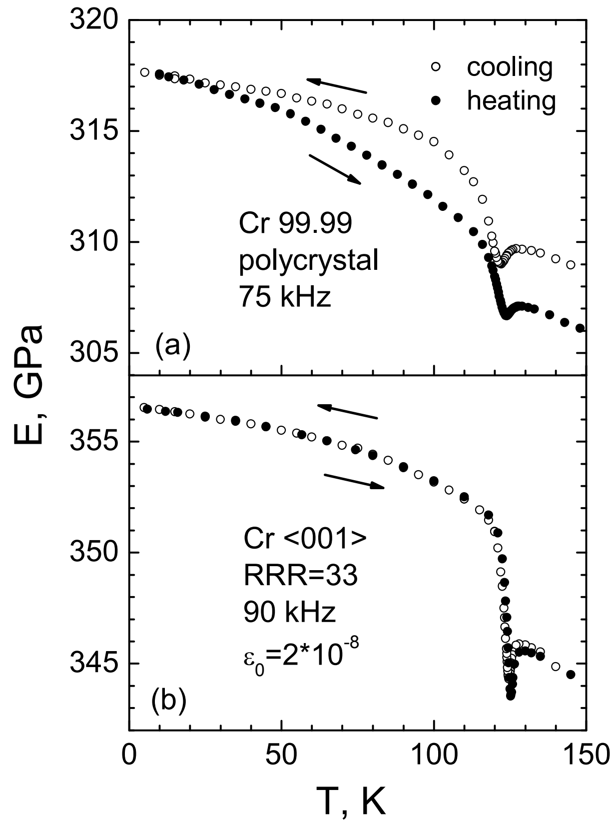

Fig. 1. Temperature dependences of the dynamic Young's modulus measured in the vicinity of the spin-flip transition in the Cr polycrystal (a) and <001> single crystal (b) (see [2]) during thermocycling at a rate of 0.1 K/min.

Results and discussion

Hysteresis of acoustical properties of polycrystals. In [2 – 4] the acoustic properties of pure single crystals of two different orientations were investigated at frequencies of 90 kHz. To establish an influence of grain boundaries on the elastic and inelastic properties, it was interesting to receive analogous data on chromium polycrystals of technical purity using the same experimental technique. As earlier, the main attention was paid to the temperature regions close to the magnetic phase transitions. The results related to the temperature changes in the dynamic Young’s modulus E in as-received polycrystalline sample are shown in Fig. 1 and

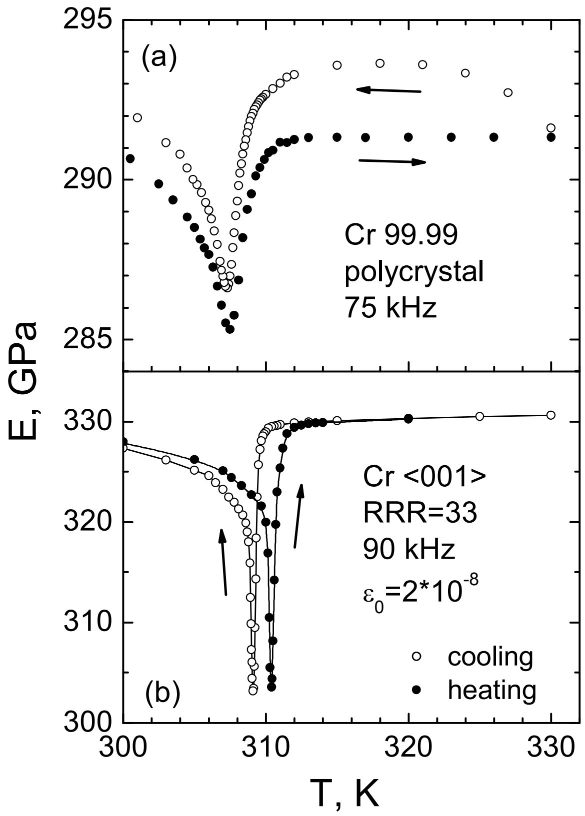

Fig. 2. Acoustic anomalies on the temperature dependences $E(T)$ near the Néel point in the Cr polycrystal (a) and <001> single crystal (b) [2] at thermocycling with a heating-cooling rate 0.1 K/min.

Fig. 2 together with the corresponding data obtained on single crystals. It can be seen that the temperature dependences E (T) obtained with the polycrystals agree qualitatively with those obtained with the single crystals. However, there are also some distinctions. The most interesting effect, that was not observed earlier, is a significant counterclockwise hysteresis of the acoustic properties that takes place when thermocycling the as-received polycrystalline samples. On cooling, the values of the dynamic Young's modulus are appreciably higher than at heating. Hysteretic behavior is observed over the whole temperature range studied. The hysteresis loop closes itself at temperatures about 330 K; this effect is reversible and can be observed again during repeated termocycling. The critical points of the acoustic anomalies near T_N and T_{SF} are somewhat lower on cooling than on heating. In the single crystals, hysteretic behavior was observed only near the phase transition points and appeared as a shift of the anomaly temperatures. In all cases the anomalies are more pronounced in single crystals than in polycrystals.

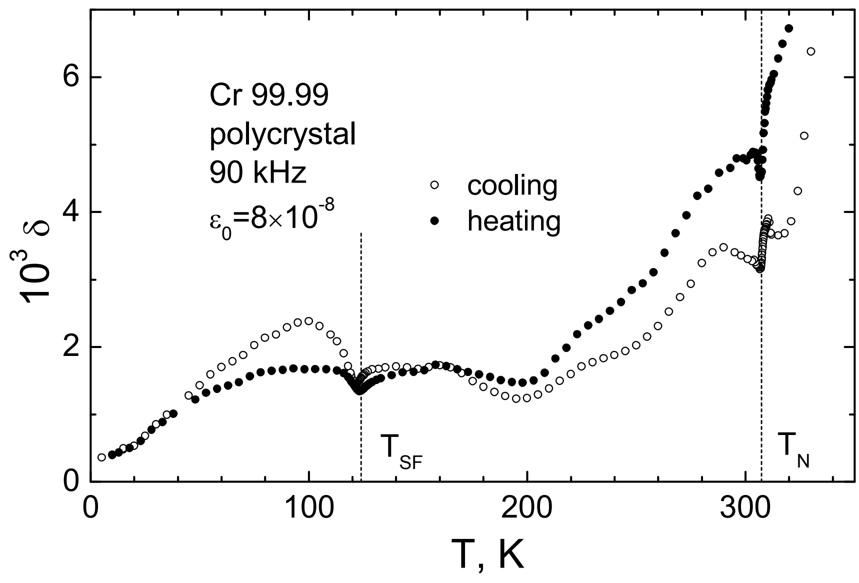

Fig. 3. Hysteresis in the temperature dependence of the decrement $\delta(T)$ in a polycrystalline sample measured at a frequency of 90 kHz: ○ – cooling, ● – heating.

Temperature dependences of the decrement $\delta(T)$ at high-frequencies exhibited several distinctive features. In particular, no internal friction peak was found at the Néel point T_N at 90 kHz for polycrystals whereas it was observed for single crystals. On the other hand, hysteretic behavior in the dependences $\delta(T)$ is more complicated (see Fig 3). At a temperature of 160 K, an inversion of the effect is observed. At temperatures above 160 K, the counterclockwise hysteresis turns into a clockwise one. As in the case of the dynamic Young's modulus, the hysteresis loop closes on heating to 330 K.

The behavior of the observed acoustic properties may be caused by changes in the AFM domain structure of the Cr polycrystals which may occur under the action of thermoelastic stresses originated from the anisotropy of the thermal expansion of quasirandomly oriented crystallites of orthorhombic and tetragonal phases of Cr. Significant accommodation stresses may appear in a polydomain structure of the Cr crystal due to the pronounced anisotropy of the lattice parameter at $T < T_{SF}$. The appearance of stretched and compressed zones with a complicated distribution of internal stresses should result in a specific distribution of domains with different orientations of the spin density wave vectors that differs from a distribution in unstressed crystals [7 – 9].

Influence of heat treatments. To clarify a role of the defect structure on the acoustic anomalies, the effect of the quenching temperature and subsequent annealing of the polycrystalline samples has been studied at the frequencies $0.6 < f < 1.5$ kHz. After quenching from 1173 to 1373 K, at temperatures just below the Néel point a bimodal peak of internal friction was observed (Fig. 4 gives example for quenching from 1273 K, circles). Location of the peak did not appreciably depend either on the quenching temperature or on the vibration frequency. After annealing, the peak height increased and in most cases the peak took an unimodal shape (up triangles). Unimodal shape of the peak was also observed after quenching from 1523 K.

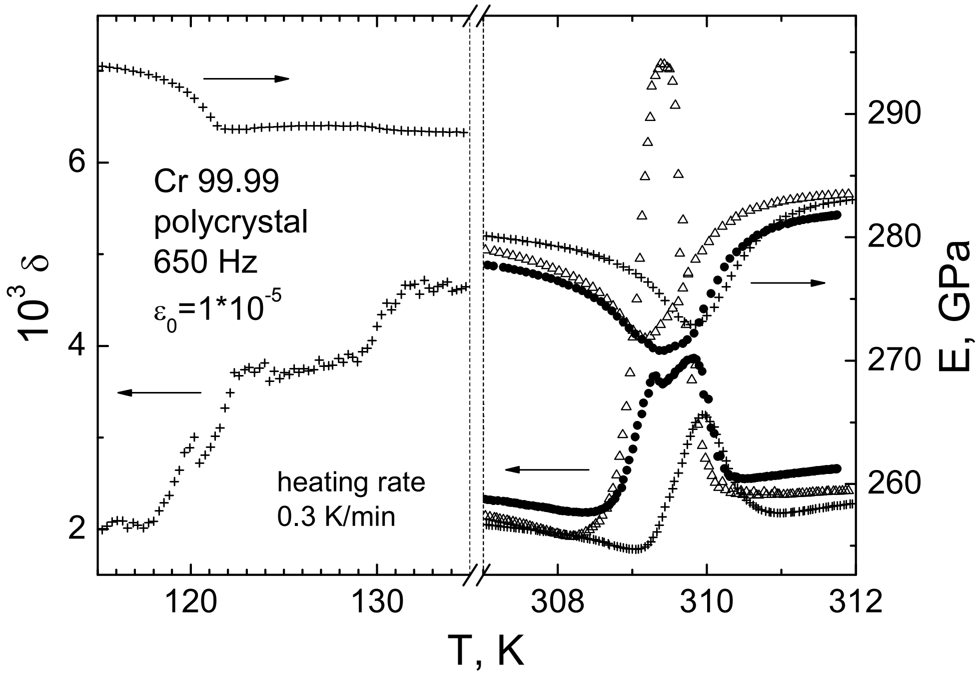

Fig. 4. Effect of heat treatments on the behavior of the decrement and the Young's modulus near the Néel point and variation of the low-frequency acoustic properties in the vicinity of the spin-flip transition: ● – after quenching from 1273 K, + – after quenching from 1523 K, Δ - after quenching from 1273 K and subsequent annealing at 733 K for 2 hours.

The effect of quenching and annealing of the polycrystalline samples correlates rather well with the results obtained on the plastically deformed and aged Cr single crystals of different orientations. Small preliminary plastic deformation of the samples (up to 1 %) led to broadening and splitting of the acoustic anomalies in the dependences $\delta(T)$ and $E(T)$ in the vicinity of the Néel point (see Fig. 5). The anomalies shifted towards higher temperatures. Near the spin-flip temperature T_{SF}, splitting of the anomalies due to plastic deformation did not occur although the dip-like anomaly in the $E(T)$ curve becomes less pronounced.

Ageing of the samples for one year at room temperature restores the width of the peak at the Néel point, but bimodality and the new average location temperature of the anomalies still remain.

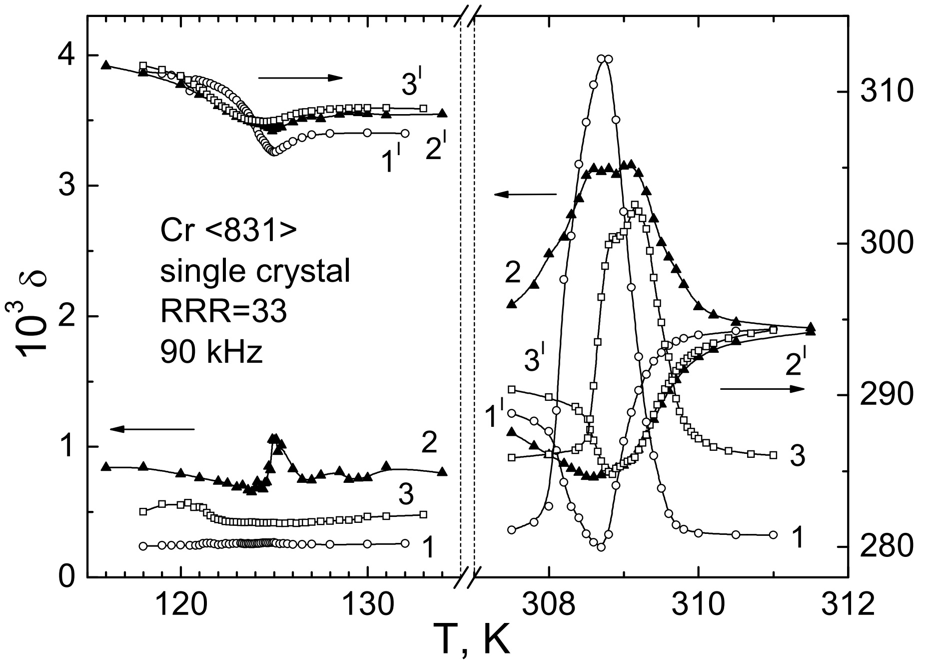

Fig. 5. Effect of plastic deformation on the dependences $\delta(T)$ (curves 1 to 3) and $E(T)$ (curves 1' to 3') in the vicinity of the Néel point and the spin-flip transition: ○ – undeformed specimen, ▲– after a plastic deformation, ε_{pl} = 1 %, at room temperature, □ - after plastic deformation, ε_{pl} = 1 %, and subsequent ageing at room temperature for 1 year.

Taking into account that most of the physical properties are sensitive to the presence of lattice defects, it is naturally to expect that an increase in the density of the crystal defects takes place during plastic deformation would entail significant changes in these properties. Both in the case of quenching and preliminary deformation, a considerable number of deformation defects should be produced in the samples. Dislocations and deformation point defects are the main types of defects produced during plastic deformation. Internal stresses associated with deformation defects may essentially change the Cr thermodynamic properties in the vicinity of the magnetic phase transitions. Conditions for the formation of ordered regions in disordered crystal containing dislocations at temperatures slightly above the critical point have been discussed in [10]. It has been shown that such pre-ordered regions could form a randomly spaced skeleton penetrating the entire crystal but occupying only a small fraction of its volume. When decreasing temperature, the thickness of the ordered skeleton branches increases and the phase transition spreads gradually over the entire crystal volume. This should lead to smearing of a phase transition and to its shift towards higher temperatures. For dislocation densities of about 10^9 cm^{-2}, this smearing should be of 0.3 K. In [7] a semiquantitative analysis of the influence of dislocations on the Néel point T_N in chromium has been done. The authors pointed out that the increase in the temperature and width of the transition is determined by the components of the internal stresses coincided with the vectors of the spin density waves. Estimations made in [11] have shown that for dislocation densities between 10^7 and 10^9 cm^{-2}, the increase in T_N should vary from 0.2 to 0.5 K. The estimations mentioned above are of the same order of magnitude as the increase in T_N and the broadening of the acoustic anomalies obtained experimentally in this work.

The bimodal shape of the peak at the Néel point may indicate that a bimodal distribution of internal stresses takes place in the crystals. It is interesting to note that the temperature separation of the peak components is almost the same in polycrystals and in single crystals. It does not practically depend (or slightly depend in a non-systematic way) on the vibration frequency, on the vibration amplitude, on the amount of the preliminary plastic deformation, on the quenching temperature, and seems to be some sort of fundamental parameter whose microscopic nature is to date unknown. To gain a better insight into this problem, detailed data on the domain structure of the quenched and deformed samples should be required.

Summary

In conclusion, low temperature dynamic elastic and anelastic properties of polycrystalline Cr of 99.99 % purity have been investigated in the kHz range during thermocycling within the temperature interval $5 < T < 330$ K. In as-received samples, a significant hysteresis of the acoustic properties was found for the first time when termocycling below the temperature of the spin-flip transition T_{SF}. The hysteresis loop closes at temperatures about 330 K and the effect is almost completely reversible and can be observed again during repeated termocycling.

The effect of heat treatments on the acoustic anomalies in the vicinity of the magnetic phase transitions in chromium polycrystals has also been investigated. The data obtained in the present work correlate rather well with the data on the influence of small preliminary deformation and long-time ageing at room temperature on the acoustic anomalies in Cr single crystals obtained earlier.

The observed behavior of the acoustic properties may be caused by transformations in the antiferromagnetic domain structure in tetragonal and orthorhombic phases under the action of stresses due to thermocycling, quenching or plastic deforming the Cr samples.

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