Magnetoelasticity of a Cr + 2.2 at.% Al-alloy single crystal

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Abstract. The temperature dependences of the elastic constants and thermal expansion of a Cr–Al-alloy single crystal containing 2.2 at.% Al are reported. This is a critical concentration, being simultaneously close to the very steep incommensurate–commensurate spin-density wave transition line on the magnetic phase diagram as well as to the triple point, where the incommensurate and commensurate spin-density wave states coexist with the paramagnetic state. Very large magnetic contributions at 0 K of up to 28% for $c_L = \frac{1}{2}(c_{11} + c_{12} + 2c_{44})$, 24% for c_{11} and 48% for the adiabatic bulk modulus, B, were observed, while the magnetic contributions to the shear elastic constants, c_{44} and $\frac{1}{2}(c_{11} - c_{12})$, amount to less than 1% at 0 K. The magnetovolume, the longitudinal elastic constants as well as B vary linearly with temperature over a large temperature range. This cannot be explained by existing theories. The absolute value of the zero-temperature magnetic Grüneisen parameter is exceptionally large, reflecting the much larger magnetic contribution to B than to the volume of the crystal at 0 K.

1. Introduction

The Cr–Al alloy system has remarkable physical properties. It has the largest absolute values of the magnetic Grüneisen parameters, the highest observed values for the Néel temperature (T_N) and the largest spin-density wave (SDW) amplitude of all Cr-alloy systems studied so far [1]. The magnetic phase diagram of this system contains four magnetic phases: the longitudinal (L) incommensurate (I) SDW phase, the transverse (T) ISDW phase, the commensurate (C) SDW phase and the paramagnetic (P) phase [1]. There exists a triple point on the magnetic phase diagram near 2 at.% Al and 130 K where the ISDW, CSDW and P phases coexist [1,2]. A plot of the magnetic Grüneisen parameters as a function of Al concentration, determined from elastic constant and thermal expansion measurements on polycrystalline Cr–Al alloys [3], shows a gigantic peak centred at 2.2 at.% Al, which is close to the triple-point concentration. This behaviour has not yet been explained.

The studies on polycrystalline material are of limited value in gaining an insight into the magnetic effects of Cr–Al alloys. This is particularly so for magnetoelastic effects for which polycrystalline measurements give incomplete information concerning the influence of the SDW on the elastic properties. Elastic constant measurements on Cr–Al alloy single crystals containing 1.2, 1.9 and 2.6 at.% Al were recently reported [2]. A single crystal containing the critical concentration of 2.2 at.% Al was unfortunately not studied and neither were magnetovolume effects in the above three Cr–Al-alloy single crystals.

We report elastic constant and thermal expansion measurements as a function of temperature on a Cr + 2.2 at.% Al-alloy single crystal. Large magnetic contributions, as high as $\approx 50\%$ at 0 K were observed in the longitudinal mode elastic constants. These

disappear at around 400 K. The magnetic contributions to the shear constants on the other hand, are much smaller, less than 1%, and disappear at a much lower temperature.

2. Experimental techniques

The techniques for growing the Cr + 2.2 at.% Al-alloy single crystal have been described previously [2]. The crystal was prepared with flat and parallel (110) faces for ultrasonic measurements by spark planing. The distance between the parallel faces is about 7 mm and the surface area about 45 mm^2. Standard ultrasonic techniques, phase comparison or pulse-echo overlap techniques [4, 5], were used to measure velocities for longitudinal or shear wave propagation along [110]. The sensitivity of the former technique is about 1 part in 10^3 and that of the latter about 1 part in 10^5. The error in the absolute values of the sound velocity is about 0.5%. The phase comparison method was very suitable for measuring the longitudinal mode velocities for which there were very large changes with temperature, while the pulse-echo overlap technique was employed for the shear mode velocities which show much smaller temperature effects. X- or Y-cut 10 MHz quartz transducers were bonded with Araldite epoxy resin to the crystal to generate longitudinal or shear waves respectively.

Thermal expansion measurements were made as previously using a strain-gauge technique [6]. The measurements were made relative to Cr + 5 at.% V, which remains paramagnetic at all temperatures and serves to simulate the non-magnetic component of Cr + 2.2 at.% Al [6], i.e. $(\Delta L/L)_{\text{meas}} = (\Delta L/L)_{\text{Cr}_9\text{V}_5} - (\Delta L/L)_{\text{Cr-Al}}$. The error in the absolute values of $\Delta L/L$ is about 5%, while changes of 3×10^{-7} with temperature could be detected easily. Thermal expansion was measured along [110]. Measurements were made in the temperature range 4–500 K for the ultrasonic wave velocities and in the range 4–320 K for the thermal expansion.

3. Results

3.1. Elastic constants

The elastic constants were obtained from ultrasonic wave velocities for [110] propagation using standard equations [7] for cubic crystals. The effects of thermal expansion have been neglected in calculating the elastic constants at different temperatures. Thermal expansion measurements reported in the next section, show that the correction in cooling the sample from room temperature to 4 K, where it is largest, amounts to about 0.1%, which is too small to affect the data significantly. The temperature dependences of the elastic constants $c_L = \frac{1}{2}(c_{11} + c_{12} + 2c_{44})$, $c' = \frac{1}{2}(c_{11} - c_{12})$ and c_{44}, which are directly obtained from the [110] wave propagation measurements, are shown in figure 1. Heating and cooling runs between 4 and 77 K gave the same results without any hysteresis effects.

Figure 2 shows the temperature dependences of c_{11} and the adiabatic bulk modulus $B = \frac{2}{3}(c_{11} + 2c_{12}) = c_L - c_{44} - \frac{1}{3}c'$ calculated from the data in figure 1. As c' could only be measured up to about 325 K where the ultrasonic signal for this shear mode becomes very small, the results for c_{11} and B are only shown up to this temperature. The broken curves in figures 1 and 2 represent the expected non-magnetic behaviour and were obtained as previously [2] from the temperature dependences of the elastic constants [8] of a Cr + 5 at.% V crystal that remains paramagnetic at all temperatures. The magnetic contributions

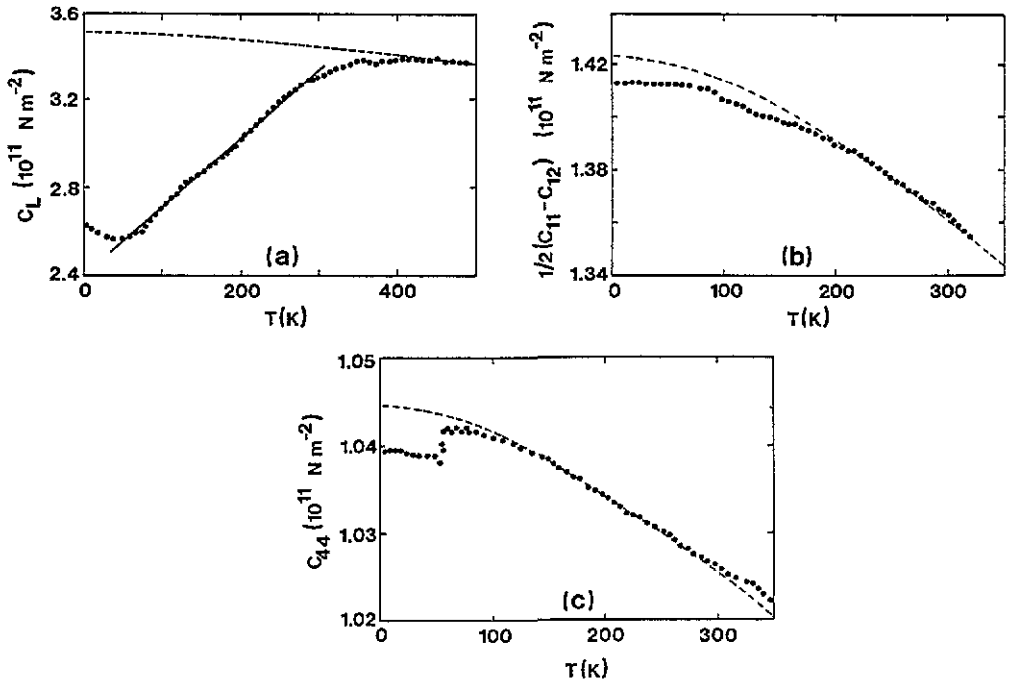$$\Delta c = c_{\text{Cr}_9\text{5}\text{V}_5} - c_{\text{Cr-Al}}$$

Figure 1. The temperature dependences of the elastic constants of Cr + 2.2 at.% Al. (a) $c_L = \frac{1}{2}(c_{11} + c_{12} + 2c_{44})$, (b) $\frac{1}{2}(c_{11} - c_{12})$ and (c) c_{44}. For clarity only about every second point is plotted. The broken curves are the expected non-magnetic behaviour determined from results of Cr + 5 at.% V. The solid line in (a) is a guide to the eye in order to emphasize the near linear temperature dependence of c_L between about 60 and 275 K.

to the elastic constants are obtained by subtracting the measured values of the Cr + 2.2 at.% Al crystal from the broken curves in figures 1 and 2. Figure 3 shows the temperature dependences of Δc_{11} and ΔB. As $\Delta c'$ and Δc_{44} are very small, we do not show them in a separate figure.

3.2. Thermal expansion

The thermal expansion

$$(\Delta L/L)_{\text{meas}} = (\Delta L/L)_{\text{Cr}_{95}\text{V}_5} - (\Delta L/L)_{\text{Cr-Al}}$$

was measured along [110] in the temperature range 4–320 K. The magnetovolume is directly given by $\Delta\omega = 3(\Delta L/L)_{\text{meas}}$. It is negative and its absolute value is shown as a function of temperature in figure 4(a). The results of Roberts *et al* [9] for the coefficient of thermal expansion ($\alpha_{\text{Cr}_{95}\text{V}_5}$) of Cr + 5 at.% V were used to calculate the coefficient of thermal expansion ($\alpha_{\text{Cr-Al}}$) of the Cr + 2.2 at.% Al crystal from $(\Delta L/L)_{\text{meas}}$ The results are shown in figure 4(b). Also shown in figure 4(b) is $\alpha_{\text{Cr}_{95}\text{V}_5}$ which simulates [10] the non-magnetic component of $\alpha_{\text{Cr-Al}}$. $\alpha_{\text{Cr-Al}}$ is shown as a smooth curve in figure 4(b). The scattering of the calculated $\alpha_{\text{Cr-Al}}$ values around this curve is within $\pm 0.1 \times 10^{-6}$ K^{-1}. Heating and cooling runs from 4 to 100 K show no hysteresis effects in $(\Delta L/L)_{\text{meas}}$.
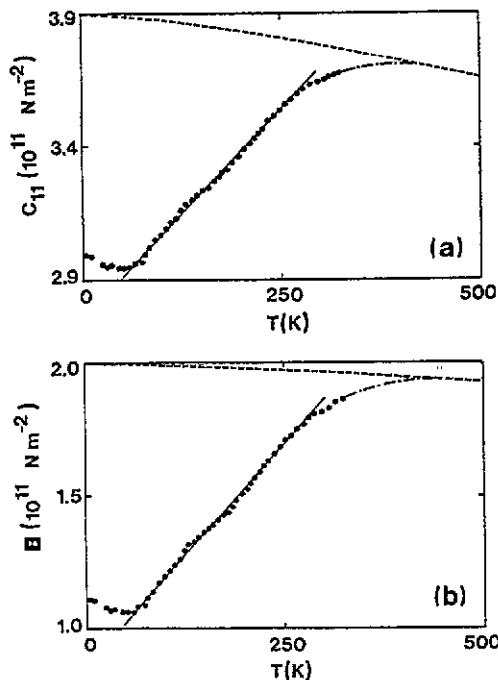
Figure 2. Temperature dependence of the elastic constant c_{11} and the adiabatic bulk modulus, B, for Cr + 2.2 at.% Al calculated from the results in figure 1. The broken curves are the expected non-magnetic behaviour determined from results of Cr + 5 at.% V and the chain curves are extrapolations of the data to higher temperatures (see also figure 1(a)). The solid lines are guides to the eye in order to emphasize the near linear behaviour between about 60 and 275 K.
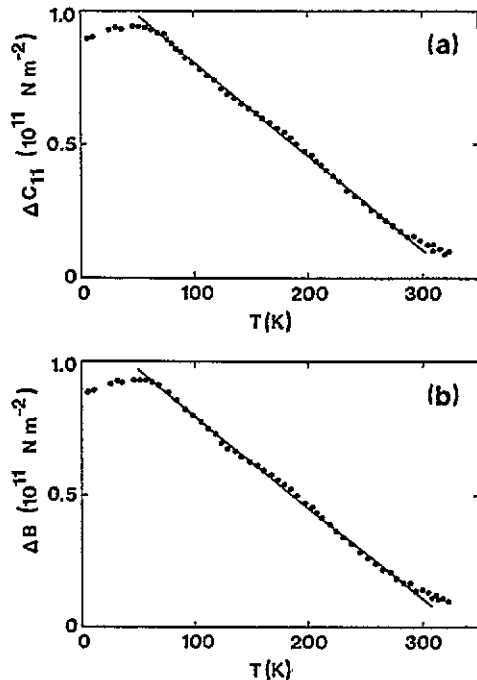
Figure 3. Temperature dependence of the magnetic contribution of (a) Δc_{11} to c_{11} and of (b) ΔB to B for Cr + 2.2 at.% Al. The solid lines are guides to the eye in order to emphasize the near linear behaviour between about 60 and 275 K.

4. Discussion

The longitudinal mode elastic constants c_L and c_{11} as well as B show very large contributions of magnetic origin below 400 K (figures 1 and 2). These contributions reach values as high as 28% for c_L, 24% for c_{11} and 48% for B at low temperatures. The magnetic contributions to the shear constants c_{44} and c', on the other hand, are much smaller, being only about 0.5% for c_{44} and 0.7% for c' at 0 K (figure 1). Furthermore, these magnetic contributions appear only at temperatures below about 100 K for c_{44} and below about 200 K for c', which is much lower than the temperature of 400 K below which the magnetic effects in the longitudinal mode constants start to set in. Magnetic effects seem to disappear somewhere between 100 and 150 K in the thermal expansion of Cr + 2.2 at.% Al (figure 4).

The determination of T_N for dilute Cr alloys from the anomalies in the magnetoelastic properties on the c–T and α–T or $\Delta L/L$–T curves can be problematic. There is presently no theoretical work that predicts the exact character of the anomalies near T_N on these curves. Usually [1] the temperature dependence of the electrical resistivity (ρ) is used to obtain T_N, which is defined at the temperature of the minimum in the $d\rho/dT$–T curves. In some cases, like for instance Cr–Co alloys [11], the temperature of the minimum on the
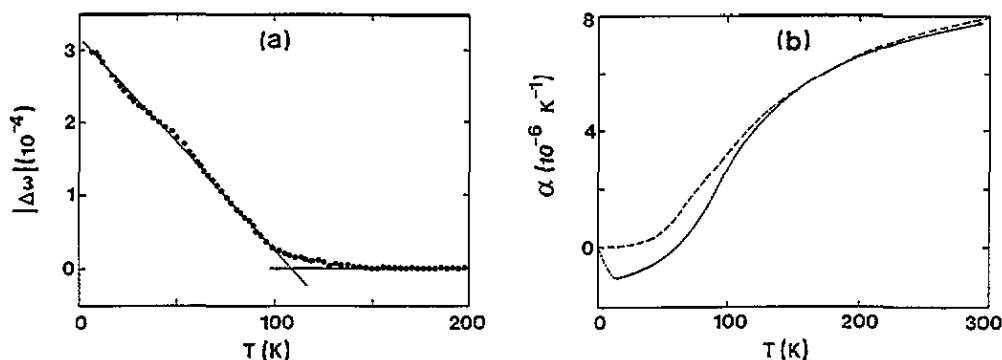
Figure 4. Temperature dependence of (*a*) the absolute value of the magnetovolume, $\Delta\omega$, and of (*b*) the coefficient of linear thermal expansion, α, for Cr + 2.2 at.% Al. The solid curve in (*b*) was calculated from figure 4(*a*). The scattering of the calculated data points around the smooth curve is within 0.1×10^{-6} K^{-1}. The broken curve in (*b*) represents the expected non-magnetic behaviour determined from results of Cr + 5 at.% V while the chain curve is a guide to the eye in extrapolating the results down to 0 K. The solid line in (*a*) is a guide to the eye in order to emphasize the near linear behaviour of $|\Delta\omega|$.

B–T curves agrees with the minimum of $d\rho/dT$. In other cases like Cr–Al [2] and Cr–Ru [12] on the other hand, the temperature at the inflection point at the sharp rise to the right of the deep minimum on the c_{11}–T, c_L–T or *B–T* curves, corresponds better with T_N as determined from neutron diffraction measurements. In the case of the thermal expansion, T_N is sometimes taken [13] at the sharp minimum on the α–T curves or in some other cases [14] at the inflection point to the right of the minimum on these curves. In the present case of the Cr + 2.2 at.% Al crystal, fixing T_N in figures 1, 2 and 4 seems even more problematic. The reasons are twofold. Firstly, the fact that magnetic effects persist for c_L to much higher temperatures than for $\Delta\omega$ (figures 1 and 4). Spin fluctuations contribute to c_L and $\Delta\omega$ above T_N [1] and probably contribute differently to these two properties, resulting in a different temperature where the magnetic contributions to each disappear. As it is presently not known how to separate the effects of spin fluctuations from the measured values of c_L and $\Delta\omega$, the temperature at which magnetic effects disappear in these two properties is not useful in obtaining T_N. Secondly, although there is a broad minimum in c_L at about 50 K which corresponds roughly with the temperature where c_{44} shows a step-like anomaly, there is, however, no indication of an anomaly in $\frac{1}{2}(c_{11} - c_{12})$, $\Delta\omega$ or in α near this temperature, making an identification of T_N with the minimum in c_L or with the step in c_{44} also problematic.

In all other Cr-alloy systems thus far studied an anomaly was observed in the α–T curves near T_N and one also expects this to happen for the Cr + 2.2 at.% Al crystal. In polycrystalline Cr + 2.19 at.% Al a small anomaly in the form of a small dip in α–T was indeed observed near 215 K [10] which corresponds to the temperature at the inflection point to the right of the minimum which was observed on the *B–T* curve for the same polycrystal. As can be seen in figure 4, there is, however, no indication of such an anomaly in the α–T curve of figure 4 for the Cr + 2.2 at.% Al crystal. We presently do not know the exact reason for the difference in behaviour between the single and polycrystalline samples. A possible explanation may perhaps be found in the fact that the concentration of 2.2 at.% Al is situated at a very unstable position on the magnetic phase diagram (see later). Furthermore, the temperature behaviour in figures 1 and 2 of c_L, c_{11} and B above the

minimum is very nearly linear between 60 and 275 K, making it impossible to determine an 'inflection' point above the minimum, as was done for polycrystalline Cr + 2.19 at.% Al [10].

The magnetovolume $|\Delta\omega|$ in figure 4 also decreases nearly linearly from the lowest temperature up to 100 K. It extrapolates to zero at about 110 K. This is in contrast with the behaviour of c_L, c_{11} and B for which the linear temperature behaviour stretches from 60 K up to 275 K, giving an extrapolated value of zero for c_L, c_{11} and B at 330 K, much higher than the temperature of 110 K obtained from the $|\Delta\omega|$ measurements. Taking all the above into account, we are therefore not able to pinpoint T_N without any doubt on the experimental curves of figures 1–4.

Another point of importance for the present crystal is the fact that its concentration is very close to the ISDW–CSDW phase transition line on the magnetic phase diagram. This transition line is very steep near 2.2 at.% Al [1, 2] in the temperature–concentration plane, and one would thus expect mixed regions of ISDW and CSDW phases in the crystal due to the slightest variation of concentration throughout its volume. In Cr–Al single crystals that are purely in the ISDW phase at all temperatures below T_N (concentrations well below the triple point), Baran *et al* [2] observed magnetic effects, probably due to spin fluctuations, that persist for c_{11}, B and c_L to well above T_N. For instance for Cr + 1.9 at.% Al with $T_N = 134$ K, these effects persist in a temperature range of about 320 K above T_N up to 450 K (their figure 2(*b*)), which is of about the same temperature range for which they persist in pure Cr [15], that is ISDW at all $T < T_N$. On the other hand, magnetic effects persist over a much smaller temperature range, of only about 150 K or smaller above T_N, in Cr–Al single crystals that are purely in the CSDW phase (see figure 2(*c*) of reference [2] and figure 3 of reference [10]). Magnetic effects persist for c_{11}, c_L and B in the Cr + 2.2 at.% Al crystal (figures 1 and 2) to temperatures well above the minimum (at 50 K) up to about $T = 450$ K, a temperature range that is more representative of that observed for ISDW than for CSDW Cr–Al alloys. The conclusion is therefore made that the present crystal appears to be predominantly in the ISDW phase. The fact that a minimum is observed in c_L, c_{11} and B and also a small step in c_{44} near 50 K, probably points to an actual T_N for the Cr + 2.2 at.% Al crystal if it was purely in either the ISDW or the CSDW state, that is much lower than $T_N = 215$ K obtained from the polycrystalline measurements on Cr + 2.19 at.% Al [10]. This will make the minimum on the phase transition line of the magnetic phase diagram, given in references [1] and [2], much sharper and deeper. Magnetic effects in the shear constants of the Cr + 2.2 at.% Al crystal are very small.

The linear decrease of $|\Delta\omega|$ for the Cr + 2.2 at.% Al crystal (figure 4) from the lowest temperature up to near the temperature where it disappears, is presently not understood. For dilute Cr alloys one expects the magnetovolume to follow the temperature dependence of the mean-square magnetization [1] and it should be surprising if this decreases linearly with increasing temperature all the way from 0 K up to the temperature where it disappears. The fact that the concentration of this crystal is so close to the ISDW–CSDW transition line on the magnetic phase diagram and probably also to the actual triple point where the ISDW, CSDW and P phases coexist [1, 2], places it at a very unstable position which may contribute to the 'apparent' linear variation of $|\Delta\omega|$, c_L, c_{11} and B observed with temperature.

There is at present no microscopic theory available to explain the observed magnetoelastic behaviour of SDW Cr alloys [1]. Some success has, however, been obtained using a thermodynamic model under the assumptions that the magnetic free energy is separable from the total free energy and that volume strain terms in the free energy dominate shear strain effects [1]. The last assumption is nearly valid for the present Cr + 2.2 at.% Al crystal, since magnetic contributions to the shear constants c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ are negligible

compared with that observed for the longitudinal constants c_L and c_{11}. The thermodynamic model has good success for Cr–Al single crystals containing 1.2, 1.9 and 2.6 at.% Al [2], and one would also expect this to be the case for the present crystal. The model predicts [1] that

$$\Delta B = B_{\text{non-magn}} - B_{\text{Cr alloy}} = B_{\text{Cr}_{95}\text{V}_5} - B_{\text{Cr–Al}}$$

should always be positive. This is observed to be the case for the Cr–Al single crystals studied by Baran *et al* [2] and also for the present Cr + 2.2 at.% Al crystal. It also predicts [1] that the sign of the magnetic contribution to α

$$\Delta\alpha = \alpha_{\text{non-magn}} - \alpha_{\text{Cr alloy}} = \alpha_{\text{Cr}_{95}\text{V}_5} - \alpha_{\text{Cr–Al}}$$

should be opposite to that of dT_N/dP, where P is the applied pressure, as is observed for polycrystalline Cr–Al alloys [10] with concentrations below 2 at.% Al for which dT_N/dP was measured directly. For the present crystal $\Delta\alpha$ is also positive (figure 4) but dT_N/dP cannot be obtained due to the problems of determining T_N as explained above. Other physical properties such as the electrical resistivity are also not useful in obtaining dT_N/dP for this Al concentration [2, 10].

A further prediction of the theory is that both ΔB and $\Delta\omega$ would vary below T_N as $a + bt^2 + ct^4$ [6], where a, b and c are constants and $t = T/T_N$. This was found [2] to be approximately valid for the elastic constants of Cr–Al single crystals containing 1.2, 1.9 and 2.6 at.% Al and also for the magnetovolume [10] of polycrystalline Cr–Al alloys. As T_N could not be determined unambiguously in the present study, we are not able to analyse the temperature dependence of $\Delta\omega$ and ΔB for the Cr + 2.2 at.% Al along these lines. It may, however, be noted from figure 4 that the observed almost linear temperature dependence of $\Delta\omega$ cannot be explained by the thermodynamic model.

The zero-temperature Grüneisen parameter, Γ_0, is defined [1, 16] by

$$\Gamma_0 = \frac{1}{B_0}\frac{\Delta B(0)}{\Delta\omega(0)} = -\frac{\phi''}{\phi'}$$

where B_0 is the bulk modulus at 0 K (taken as the average between that of the reference material, Cr + 5 at.% V, and the sample), $\Delta B(0)$ and $\Delta\omega(0)$ are, respectively, the magnetic contributions to B and the magnetovolume at this temperature and ϕ' and ϕ'' are, respectively, the first and second derivatives of volume strain of the magnetic free energy at 0 K. A value $\Gamma_0 = -1890$ is obtained for the Cr + 2.2 at.% Al single crystal from figures 2 and 4. This is substantially smaller than the value $\Gamma_0 = -1300$ obtained [3] for polycrystalline Cr + 2.19 at.% Al, which shows a peak in $|\Gamma_0|$ at this concentration and is also much smaller than the value $\Gamma_0 = -70$ for pure Cr [16]. One thus has $|\phi''| \gg |\phi'| \approx 2000|\phi'|$ at this peak concentration.

The magnetic contribution to the coefficient of volume thermal expansion ($\Delta\beta$) is $\Delta\beta = (d/dT)(\Delta\omega) = 2.9 \times 10^{-6}$ which remains constant for the Cr + 2.2 at.% Al crystal between 4 K and about 100 K, becoming zero at $T \geqslant 120$ K (figure 4(*a*)). This, together with the linear temperature variation observed for $\Delta B(T)$ between 60 and 275 K (figure 3(*b*)) and the fact that T_N could not be obtained, does not allow for a determination of the other two magnetic Grüneisen parameters defined by [3]

$$\Gamma_{\text{NT}} = -\frac{1}{B_N T_N}\lim_{t \leqslant 1}\left(\frac{\Delta B(t)}{\Delta\beta(t)}\right)$$

and

$$\Gamma_{\text{sf}} = -\frac{1}{B_N T_N}\lim_{t \geqslant 1}\left(\frac{\Delta B(t)}{\Delta\beta(t)}\right)$$

for the present Cr + 2.2 at.% Al crystal as was done previously, for instance for Cr–Si-alloy single crystals [6].

5. Conclusions

Elastic constants and thermal expansion of a Cr–Al-alloy single crystal containing the critical concentration of 2.2 at.% Al were studied for the first time. The sharp linear increase in c_L, c_{11} and B (at a rate of 3.2×10^8 N m^{-2} K^{-1} for each) with increasing temperature in the range 60–275 K, as well as the linear decrease of the magnetovolume, $|\Delta\omega|$, (at a rate of 2.9×10^{-6} K^{-1}) from 4 to 100 K, cannot be explained at present. It was not possible to determine T_N unambiguously from the present measurements. The results nevertheless point to the possibility of T_N being much lower than the value previously obtained for polycrystalline Cr alloys, making the minimum on the phase transition line of the magnetic phase diagram much deeper and sharper. The observed temperature dependence of the elastic constants and magnetovolume is not explained by the existing thermodynamic model. The absolute value of the zero-temperature magnetic Grüneisen parameter is extremely large, emphasizing the fact that magnetic effects are much larger in the bulk modulus of this crystal than in its volume at 0 K. It is suggested that the observed temperature dependence of the magnetoelasticity and magnetovolume of the Cr + 2.2 at.% Al crystal is in some way related to the fact that its concentration is situated at an 'unstable' position on the magnetic phase diagram, being simultaneously very close to the steep ISDW–CSDW magnetic phase transition line and also close to the triple point where the ISDW, CSDW and P states coexist.

Acknowledgments

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