Magnetic properties and magnetic phase transitions in the hydride $Gd_2Co_7H_{7.7}$

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The crystal structure, magnetic moment, magnetocrystalline anisotropy, magnetostriction, hysteresis magnetic properties and magnetic phase transitions of the hydride $Gd_2Co_7H_{7.7}$ have been investigated. An explanation is given for the observed variations in the magnetic properties and the magnetic phase transitions when the initial compound Gd_2Co_7 is hydrogenated.

1. INTRODUCTION

It is known[1-3] that the absorption of hydrogen by intermetallic compounds of the rare earth metals (R) with 3*d* transition metals (T) leads to a great change in their crystal structure, magnetic and electric properties. The intermetallides R_nT_m, compounds of the type R_2Co_7 include convenient materials for studying the effect of absorption of hydrogen on their magnetic properties, since they absorb an appreciable quantity of hydrogen at moderate pressures and temperatures, forming hydrides which are stable at room temperature. The general drawback in studying the magnetism of hydrides of R_nT_m compounds lies in the fact that measurements of the physical properties are carried out on powder specimens, since the alloys are usually broken up on hydrogenation. This complicates the interpretation of phenomena observed on hydrides of R_nT_m compounds.

In the present work results are given for the first time of a study of the crystal structure, magnetic properties and of the magnetic phase transitions in the hydride $Gd_2Co_7H_{7.7}$, made on single-crystal specimens.

2. EXPERIMENTAL METHOD

The Gd_2Co_7 alloys were obtained by melting Gd (99.9) and Co (99.99) in an induction furnace in a helium atmosphere. They were then remelted in a resistance furnace to produce a large-grained state. According to metallographic and x-ray analysis, the alloys contained less than 3% of extraneous phases. Single-crystal specimens were cut out of large grains of the ingot, in the shape of approximately 2 mm diameter disks. According to x-ray results, the disorientation of subgrains in the specimens used for the investigation was less than 3°. The specimens were then outgassed in a vacuum of 0.133 Pa at a temperature of 470 K for 1.5 h and hydrogenated at this temperature at a hydrogen pressure of 1.33×10^3 Pa. Cooling of the specimens to room temperature was carried out in the presence of hydrogen. The hydrogen content was determined from the change in specimen mass.

The single-crystals maintained their shape after hydrogenation. Since the specimens were unstable, they were immediately sealed with epoxy resin after hydrogenation for measurement of their magnetic properties at different temperatures.

The thermal expansion of Gd_2Co_7 and $Gd_2Co_7H_{7.7}$ single-crystals was studied in the temperature range 5–320 K using an x-ray diffractometer with Fe K_α radiation. The crystal lattice parameters *a* and *c* were determined from the (400) and (00.39) reflections. The uncertainty in measuring the lattice parameters was 10^{-4}.

Measurements of the magnetic characteristics was carried out using a vibration magnetometer with d.c. magnetic fields in an electromagnet up to 22 kOe, in the temperature range 4.2–800 K, and in a superconducting solenoid at 4.2–320 K in magnetic fields up to 60 kOe. The uncertainty in measuring magnetization was 3%. Transverse magnetostriction was measured in pulsed fields up to 100 kOe, applied along the *c* axis, using a quartz transducer stuck to the basal plane of the specimen with epoxy resin. The absolute uncertainty was 30%, the relative uncertainty 5%; it should be noted that the great fragility of the specimens can appreciably lower the absolute value of the magnetostriction.

3. CRYSTAL STRUCTURE

As is known,[4] the intermetallic compound Gd_2Co_7 has a rhombohedral crystal lattice of the $R\text{-}\overline{3}m$ space group Gd_2Co_7 type. The crystal lattice is preserved after this compound is hydrogenated up to the composition $Gd_2Co_7H_{7.7}$. However, the lattice parameters at room temperature increase from $a = 0.5028$ nm and $c = 3.638$ nm for Gd_2Co_7 to $a = 0.5234$ nm and $c = 3.859$ nm for $Gd_2Co_7H_{7.7}$; the lattice expansion is then anisotropic. While hydrogenation increases the parameter *a* at room temperature by 4.1%, it increases the parameter *c* by 6.3%. The volume expansion is rather large and is 15.0%. We note that after the hydrogen is pumped off for 1 h at $T = 670$ K and a pressure of 0.133 Pa, the crystal lattice parameters revert to their initial state.

The temperature dependence of the lattice parameters *a* and *c* for Gd_2Co_7 and the hydride $Gd_2Co_7H_{7.7}$ is shown in Fig. 1. The relatively narrow temperature range of measurement of the parameters *a* and *c* for the hydride is due to the desorption of hydrogen at $T > 340$ K. The $a(T)$ and $c(T)$ variations for the initial Gd_2Co_7 compound in the paramagnetic region are described by a Debye curve, departures from which for $T \leqslant 775$ K are explained by a positive spontaneous magnetostriction which arises as a result of magnetic ordering (see the inset to Fig. 1). The experimental $a(T)$ and $c(T)$ curves of the hydride $Gd_2Co_7H_{7.7}$, measured in the magnetically ordered temperature region, have two changes of shape at $T = 140$ and 240 K which are especially marked for the $a(T)$ variation. The appearance of these anomalies may be produced not only by magnetic phase transitions but

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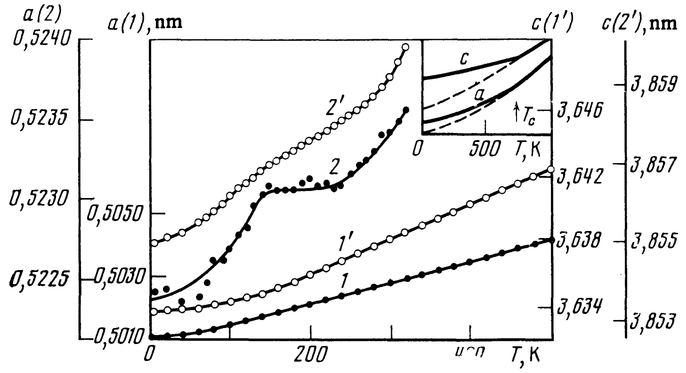

FIG. 1. The temperature dependence of the lattice parameters a and c for Gd_2Co_7 (curves 1 and 1') and for $Gd_2Co_7H_{7.7}$ (curves 2 and 2'). The inset shows the temperature dependence of a and c for Gd_2Co_7 over a wide temperature range.

also by hydrogen ordering processes or its redistribution among the interstitial positions. Such hydrogen transformations have been observed in hydrides of cubic Laves phases in the same temperature region,[5] and it is not impossible that this is true for the hydride $Gd_2Co_7H_{7.7}$.

4. MAGNETIC MOMENT

The temperature dependence of the magnitudes of the molecular magnetic moment μ_m of Gd_2Co_7 and $Gd_2Co_7H_{7.7}$ single-crystals is shown in Fig. 2, obtained by extrapolations to $H=0$ of the downward branches of the hysteresis loops, measured when a magnetic field is applied along the axis of easy magnetization (AEM$\|$**c**) at different temperatures. The most characteristic magnetization curves and hysteresis loops at several temperatures are shown in Fig. 3. As is well known,[6] the initial compound Gd_2Co_7 is a magnetically uniaxial ferrimagnetic in which, owing to the negative Gd-Co exchange interaction ($E^{\rm ex}_{\rm Gd\text{-}Co}<0$), the resulting magnetic moments of the Gd ions ($\mu_{\rm Gd}$) are oriented antiparallel to the magnetic moments of the Co ions ($\mu_{\rm Co}$). Its magnetic characteristics, according to data in Deryagin *et al.*,[6] are given in Table I.

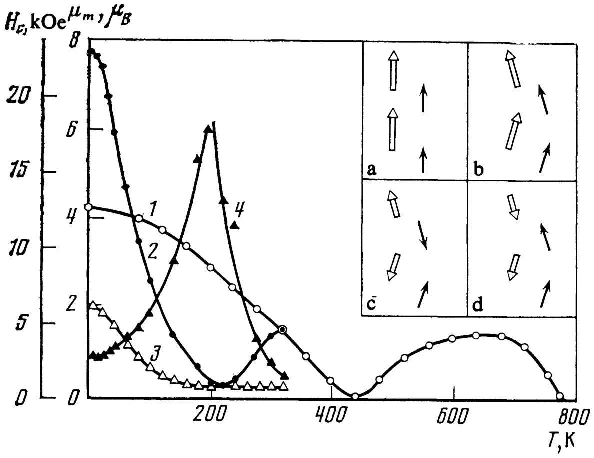

FIG. 2. The temperature dependence of the molecular magnetic moment μ_m (in units of μ_B) of single crystals of Gd_2Co_7 (1—$H=8$ kOe, **c**$\|$**H**), $Gd_2Co_7H_{7.7}$ (2—$H=20$ kOe, **c**$\|$**H**; 3—$H=20$ kOe, **c**$\perp$**H**) and the coercive force of a $Gd_2Co_7H_{7.7}$ crystal (4 — **c**$\|$**H**). The systems of magnetic structures of the hydride at different temperatures are shown in the inset: a) $4.2<T<30$ K; b) $30<T<240$ K; c) $240<T<T_N$; d) $240<T<T_N$, $H>H_c$.

A great increase in the molecular magnetic moment μ_m at 4.2 K occurs when hydrogen is introduced into Gd_2Co_7 from 4.2 μ_B for Gd_2Co_7 to 7.7 μ_B for $Gd_2Co_7H_{7.7}$. The virgin magnetization curve (Fig. 3, curve 2) is then a straight line, as for Gd_2Co_7, with a slope tangent to the ordinate axis approximately equal to the demagnetizing factor N of the specimen. As the magnetic field increases the magnetic moment μ_m reaches saturation in fields close to the demagnetizing field of the specimen NM_s, where M_s is the saturation magnetic moment (Fig. 3, curve 2). It can be concluded from this that the hydride $Gd_2Co_7H_{7.7}$ behaves at $T=4.2$ K as a typical collinear ferrimagnet in which, as in Gd_2Co_7, the moment $\mu_{\rm Gd}$ is antiparallel to $\mu_{\rm Co}$. If it is assumed that in the hydride $Gd_2Co_7H_{7.7}$ at 4.2 K, $\mu_{\rm Gd}=gJ=7\ \mu_B$ (g is the Landé factor, J is the total quantum number), then the average magnetic moment per Co atom is

$$\mu_{\rm Co}=(2\mu_{\rm Gd}-\mu_m)/7=\mu_B(14-7.7)/7=0.90\,\mu_B.$$

This value of $\mu_{\rm Co}$ is close to $\mu_{\rm Co}=0.93\ \mu_B$ in the isostructural hydride $Y_2Co_7H_6$ (Ref. 7). However, it is appreciably

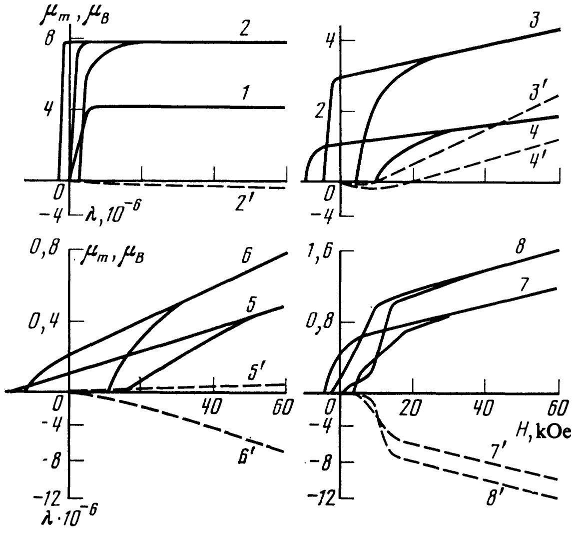

FIG. 3. Hysteresis loops along the c axis of single crystals of Gd_2Co_7 (1 — 4.2 K) and $Gd_2Co_7H_{7.7}$ (curves 2–8) and magnetostriction λ isotherms of a $Gd_2Co_7H_{7.7}$ single crystal (curves 2'–8') for different temperatures: 2, 2') 4.2 K; 3, 3') 80 K; 4, 4') 140 K; 5, 5') 200 K; 6, 6') 240 K; 7, 7') 270 K; 8, 8') 320 K.

TABLE I. Crystal lattice parameters and magnetic characteristics of the compounds Y_2Co_7, Gd_2Co_7 and their hydrides.

Compound	$T=298$ K		$T=4,2$ K				T_c, K	T_N, K	T_K, K
	a, nm	c, nm	μ_m, μ_B	μ_{Co}, μ_B	H_a, kOe	$K_1 \cdot 10^{16}$, erg·mole^{-1}			
Gd_2Co_7	0,5027	3,638	4,2	1,40 *	210	40,9	775	–	440
$Gd_2Co_7H_{7,7}$	0,5234	3,857	7,7	0,90 *	77	27,5	–	420 **	200
Y_2Co_7	0,4990	3,623	9,6	1,37	105	46,7	639	–	–
$Y_2Co_7H_6$	0,5160	3,818	6,5	0,93	300 ***	90,3 ***	–	470	–

*In calculating μ_{Co} from the magnitude of μ_m it was assumed that $\mu_{Gd} = gJ = 7\,\mu_B$ (g is the Landé factor and J the total quantum number).

**The Néel temperature of this compound was estimated since desorption of the hydrogen takes place for $T > 340$ K.

***Extrapolation of the magnetization curve in the basal plane to the magnetic moment induced at the metamagnetic transition gives a value of H_a equal to the sum of the effective anisotropy magnetic field and the effective intrasublattice exchange interaction field.

lower than $\mu_{Co} = 1.40\,\mu_B$ in the compound Gd_2Co_7 and $\mu_{Co} = 1.37\,\mu_B$ in Y_2Co_7 (see Table I).

In general, the lowering of the magnetic moment of Co on hydrogenation of a $R_n\,Co_m$ compound, while not typical, is a fairly common occurrence.[3] However, there is no unique explanation of this phenomenon at present, and there are several points of view about it. They can be formulated in a way which is applicable to the present case, as follows.

1) The lowering of μ_{Co} on hydrogenation is produced by a reduction in the Gd-Co exchange and as a consequence of this by a splitting of the 3d electron band of the Co ion just as in $Gd_{1-x}Y_xCo_2$ compounds when the concentration of the nonmagnetic yttrium is increased.[8]

2) The hydrogen, on entering the Gd_2Co_7 crystal lattice, becomes a proton and gives up its 1s electron to the 3d band of cobalt with, for example, spin "down" lowering μ_{Co} (proton model). The hydrogen in this model is an electron donor.

3) The introduction of hydrogen into the crystal lattice leads to the appearance of additional low-lying 1s energy levels associated with the electronic charge near the hydrogen atoms, the filling of which leads to the emptying of electrons of the 3d subband with, for example, spin "up" and the reduction of μ_{Co} (anion model). In this model the hydrogen is an electron acceptor.

In spite of the fact (which will be shown later) that the Gd-Co exchange is actually lowered when hydrogen is introduced into the compound Gd_2Co_7, the first reason hardly has an appreciable influence in our case. This derives from the fact that the lowering of μ_{Co} from $1.40\,\mu_B$ in Gd_2Co_7 to $0.90\,\mu_B$ in $Gd_2Co_7H_{7.7}$ is practically equal to the reduction in μ_{Co} from $1.37\,\mu_B$ in Y_2Co_7 to $0.93\,\mu_B$ in the ferromagnetic state of $Y_2Co_7H_6$ (Ref. 7), although when Y_2Co_7, is hydrogenated naturally no change in the magnitude of the Y-Co exchange takes place, since it is simply equal to zero both in the initial and in the hydrogenated compound Y_2Co_7 (Y is a nonmagnetic ion).

As regards the other two models, they both explain qualitatively the reduction in μ_{Co} observed experimentally when the compound Gd_2Co_7 is hydrogenated. However, it can be concluded on the basis of theoretical calculations[9] of the electronic structure of the hyrides of the 3d metals (Ti, V, Cr), that both models, based on a rigid 3d band, are too simplified and only reflect the limiting cases of the true position. In actual fact, the introduction of hydrogen into the crystal leads to a change, sometimes radical, of the whole electron energy spectrum. The models mentioned above thus only have the right to exist until such time as actual calculations of the band structure are carried out for the compounds studied and their hydrides. According to both models a change in the electron concentration takes place on hydrogenation of the compounds and, consequently, hydrogenation besides hanging the lattice parameter, should change the exchange interaction and the nature of the magnetic ordering.

5. EXCHANGE INTERACTIONS AND MAGNETIC PHASE TRANSITIONS

We have shown earlier[7] that in the isostructural hydride $Y_2Co_7H_6$, over the whole temperature range of the magnetically ordered state ($0 < T < T_N = 470$ K) the Co-Co exchange interaction within the sublattice is negative ($E^{ex}_{Co\text{-}Co} < 0$) and the magnetic moments of the sublattices of Co atoms are aligned antiparallel (antiferromagnetically) relative to one another. This intrasublattice interaction is small in absolute value, as can be deduced from the relatively low value of the crystal field for the metamagnetic first order phase transition (≈ 25 kOe at $T = 4.2$ K) induced by an external magnetic field. It can be suggested on the basis of these facts that in the hydride $Gd_2Co_7H_{7.7}$ the intrasublattice Co-Co exchange interaction is also negative and small in absolute value. In addition, as was shown in § 4, in the process of magnetization at $T = 4.2$ K the hydride $Gd_2Co_7H_{7.7}$ behaves as a typical ferromagnet (more precisely a ferrimagnet) with a collinear magnetic structure. This apparent contradiction can easily be removed if it is assumed that in the hydride $Gd_2Co_7H_{7.7}$ at $T = 4.2$ K we have $|E^{ex}_{Gd\text{-}Co} < 0| > |E^{ex}_{Co\text{-}Co} < 0| > |E^{ex}_{Gd\text{-}Gd}|$. The ferromagnetic alignment of the Co magnetic moments at low temperature is then brought about by the strong Gd-Co exchange interaction, tending to order the ferromagnetic Co sublattice (Fig. 2,a), although it is lower in the hydride compared with the initial compound, as follows from the lower value of the compensation temperature T_c in the hydride.

With increasing temperature the role of the Co-Co antiferromagnetic exchange increases, tending to turn the moments of the Co sublattice antiparallel to one another. As a result of the competition between $E^{\text{ex}}_{\text{Gd-Co}}$ and $E^{\text{ex}}_{\text{Co-Co}}$ a noncollinear magnetic structure is realized (Fig. 2,b). It must be noted that there are two nonequivalent Gd positions in the present compound and five Co positions, so that the noncollinear magnetic structure which arises can be fairly complicated. The occurrence of the noncollinear structure at $T > 30$ K leads to an increase in molecular moment in the region of fields above technical saturation, due to deformation of the magnetic structure in a magnetic field along the c axis and the appearance of magnetostriction λ of an exchange nature (Fig. 3). At the compensation point, $T_c = 200$ K, λ changes sign since the direction of rotation of the magnetic sublattices changes (Fig. 3, curves 4–6).

It is most likely that an antiferromagnetic noncollinear structure is realized in the hydride in the temperature range $240\ \text{K} < T < T_N$, which arises because the intrasublattice Co-Co negative exchange interaction dominates the negative Gd-Co exchange interaction (Fig. 2,b). A transition to the ferrimagnetic structure (Fig. 2,c) takes place when such as antiferromagnet is magnetized along the c axis, accompanied by a correspondingly sharp rise in magnetization μ_m and a transverse magnetostriction λ (Fig. 3, curves 7 and 8). The value of the induced magnetic moment at 320 K, $\mu_m = 0.8\,\mu_B$, is 5.7 times less than for the first-order metamagnetic phase transition in the hydride $Y_2Co_7H_6$ at the same temperature. Such a difference is explained by the antiferromagnetic coupling of the Gd and Co moments and also by the noncollinearity of the magnetic structure. The formation of antiferromagnetic ordering leads to the appearance of a sharp bend in the temperature dependences of the lattice parameters a and c at $T = 240$ K (Fig. 1).

As the temperature increases, a gradual transition thus takes place in the hydride $Gd_2Co_7H_{7.7}$ from a collinear ferrimagnet to a noncollinear antiferromagnet. When the hydride is magnetized along the c axis in the antiferromagnetic state, a phase transition induced by the magnetic field is observed. Neutron diffraction studies are essential for a more detailed explanation of the change in the magnetic structure of the hydride.

6. MAGNETIC HYSTERESIS PROPERTIES

The temperature dependence of the coercive force H_c of the hydride $Gd_2Co_7H_{7.7}$, measured on magnetization in a d.c. magnetic field of 60 kOe along the AEM (c axis) is shown in Fig. 2. The value of H_c of the initial compound along the c axis at $T = 4.2$ K is about 0.1 kOe and increases to about 1 kOe at $T = T_c$, while H_c for the hydride at 4.2 K is 2.6 kOe and increases to 18 kOe at $T = T_c$. The results obtained are very interesting. The point is that H_c reaches a maximum at $T = T_c$. This is the usual behavior and it is connected with the fact that at $T = T_c$ the magnetic anisotropy field $H_a = 2K_1/M_s$, where K_1, the anisotropy constant, becomes very great in that $M_s \to 0$. The chief interest lies in the fact that hydrogenation increases H_c by a factor of almost 26 compared with the initial compound, and the whole massive specimen remains in the one-domain state after magnetization, in spite of the fact that on hydrogenation the magnetic anisotropy constant, obtained from the magnetization curves along the transverse to the c axis, decreases by about 30% and the anisotropy field by a factor of 3 (see Table I). What interferes with the process of magnetic reversal in the hydride?

From the fact that the magnetization curve along the AEM of the hydride is linear and that saturation of the magnetization is reached in a field equal to the intrinsic demagnetization field of the specimen, it follows that magnetization takes place easily by means of shifting the domain walls. Consequently, the difficulty in reversing the magnetization of the hydride $Gd_2Co_7H_{7.7}$ is mainly determined by the degree of difficulty for magnetization reversal nuclei to arise or grow (domain structure). Reverse magnetization nuclei usually arise relatively easily at a number of crystal defects, for example dislocations, stacking faults, antiphase boundaries etc, in the region of which such local magnetic characteristics as the magnetocrystalline anisotropy and the exchange parameter have lower values compared with the values for the perfect part of the crystal. This is evidently the situation in the case of Gd_2Co_7.

The situation is somewhat involved for the hydride. It is well known[10] that hydrogen introduced into the crystal lattice has a high mobility even at low temperatures, and actively surrounds dislocations or their accumulations, forming Cottrell atmospheres. As a result of this, the hydrogen concentration in the neighborhood of defects is appreciably higher than the average throughout the crystal. In the neighborhood of defects such parameters as the magnetic anisotropy constant and the exchange interaction can thus differ appreciably not only in magnitude, but also in sign. Such places can be, on the one hand, centers of very easy nucleus formation,[11] or on the other, effective barriers to the growth of nuclei of domain structure which arise as a result of the large energy density gradient of the domain walls of nuclei on their growth. Evidently, it is just the enhancement of processes interfering with the growth of nuclei of magnetic reversal that is the main reason for the growth in coercive force when the compound Gd_2Co_7 is hydrogenated and for the metastable one-domain state in bulk specimens of the hydride $Gd_2Co_7H_{7.7}$ to arise. We note that at $T = 4.2$ K this hydride has a value of the remanent induction $4\pi M_s = 5.9$ kG and maximum energy product $(BH)_{\max} = 8.1$ MG·Oe, while for the initial compound under the same conditions they are practically equal to zero. It follows from this that hydrogenation can be one of the effective means of raising the magnetic stiffness of materials for permanent magnets.

7. CONCLUSIONS

1) Single crystals of the hydride $Gd_2Co_7H_{7.7}$ have been obtained for the first time. Absorption of hydrogen leads to a 15% increase in the volume of the elementary cell without altering the crystal symmetry.

2) A reduction in the mean magnetic moment of cobalt atoms by 34% and in the magnetocrystalline anisotropy

constant by 30% compared with the initial compound Gd_2Co_7 was found.

3) It was found that absorption of hydrogen increases the coercive force of the compound as a result of an increase in processes which hinder the growth of nuclei of reverse magnetization.

4) It was established that raising the temperature, as a result of the competition between the Gd-Co exchange interaction and the negative intrasublattice Co-Co exchange which arises on hydrogenation, induces a gradual transition from a collinear ferrimagnetic ordering to antiferromagnetic via a noncollinear intermediate structure. A magnetic field applied along the *c* axis in the antiferromagnetic temperature regime induces a phase transition to a ferrimagnetic structure.

5) It was found that deformation of the noncollinear magnetic structure of the hydride when it is magnetized along the *c* aixs leads to the appearance of magnetostriction of an exchange kind which changes sign on passing through the compensation temperature.

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