ac-susceptibility anomaly and magnetic anisotropy of R_2Co_{17} compounds, with R = Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu

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The temperature dependence of the ac susceptibility, χ' and χ'', was measured in the temperature range from 4.2 to 300 K for various polycrystalline compounds R_2Co_{17}, with R=Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Lu and single-crystalline compounds R_2Co_{17}, with R=Pr, Nd, Dy, Tb, Ho, and Er. A spin-reorientation transition was traced in Pr_2Co_{17} and Nd_2Co_{17} at 180 and 175 K, respectively. An anomalous phenomenon, which was observed in R_2Co_{17} compounds, with R=Tb, Dy, and Ho, is characterized by a peak in the curve of χ' and χ'' versus T. It is deduced that the nature of this anomalous phenomenon is correlated with the magnetic anisotropy within the basal plane. This anomaly is attributed to a temperature-induced domain-wall movement under excitation of the external ac field. For the uniaxial-anisotropy compounds Er_2Co_{17} and Tm_2Co_{17}, a sharp change of the shape of the temperature dependence of the ac susceptibility was observed. No anomaly in $\chi'(T)$ and $\chi''(T)$ is detectable in Y_2Co_{17}, Ce_2Co_{17}, Gd_2Co_{17}, and Lu_2Co_{17}. The anisotropy field, H_A, of uniaxial-anisotropy Ce_2Co_{17}, Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17} has been determined by the singular-point-detection technique in the temperature range from 4.2 to 1000 K. The easy-magnetization direction of Ce_2Co_{17} is found to be along the c axis over the whole magnetically ordered temperature.

I. INTRODUCTION

In the past two decades, R_2Co_{17} compounds have been studied intensively because of their favorable magnetic properties for the production of permanent magnets. However, compared to the RCo_5 and $R_2Fe_{14}B$ series, the fundamental understanding of the physical properties of R_2Co_{17} still remains very limited. For the purpose of application, only Sm_2Co_{17} is of interest, which is mainly due to its large anisotropy field and, consequently, the high value of the realized coercivity. Therefore, many investigations have been performed on Sm_2Co_{17} and its substituted compounds (see, e.g., a review article by Strnat[1] and the papers cited therein). Following successful production of single crystals of R_2Co_{17} of reasonable size, systematic investigations of saturation magnetization and magnetic anisotropy constants were performed on various single-crystalline R_2Co_{17} at various temperatures from 4.2 to 1200 K by Deryagin and co-workers[2–6] and Kudrevatykh *et al.*[7] Many high-field magnetization measurements on various single-crystalline R_2Co_{17} at 4.2 K, with external field applied along different crystallographic directions, were performed in the High-Field Installation of the University of Amsterdam.[8–18] The most exciting result of these studies is the observation of the first-order moment reorientation phenomenon in some ferromagnetically ordered R_2Co_{17} compounds at low temperatures. Based on these studies, a direct method for determining the intersublattice exchange coefficient (n_{RT}) by high-field measurement on single crystal or on free powdered samples was developed. The magnetic properties of R_2Co_{17} can be summarized as a magnetic anisotropy phase diagram as shown in Fig. 1.

As is well known, the ac susceptibility depends strongly on the magnetic anisotropy energy. Therefore, the measurement of the temperature dependence of the ac susceptibility can be used to trace the temperature-induced magnetic transition that is caused by the change of the magnetic anisotropy energy in the R-T compounds. Previously, we have detected an anomaly in $Pr_2Fe_{14}B$, $Pr_2Co_{14}B$, $SmFe_{11}Ti$, and $SmFe_{10}Mo_2$ and an additional peak (different to the peak caused by the spin-reorientation transition) in $Nd_2Fe_{14}B$ $Nd_2Fe_{14}C$, and $Nd_2Co_{14}B$ by measuring the temperature dependence of

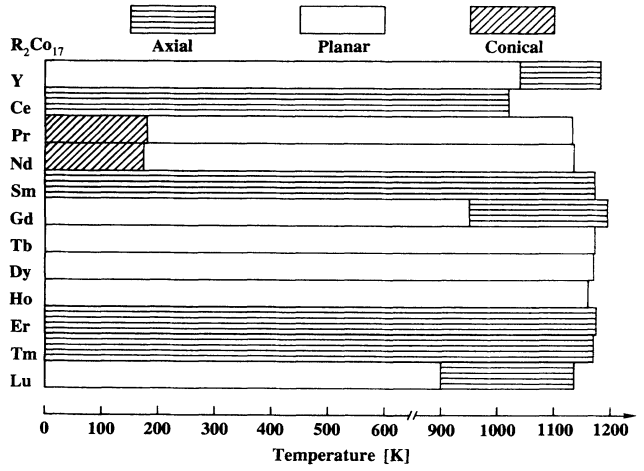

FIG. 1. Magnetic anisotropy phase diagram of R_2Co_{17} compounds.

the ac susceptibility.[19,20] This peak depends, moreover, upon the crystallographic directions, which means that such a peak will disappear when the external field is applied parallel to some specific crystallographic directions. The physical nature of this peak remains unclear to date. A similar phenomenon is also possible in other R-T compounds. In the present investigation, we report a systematic study of R_2Co_{17} compounds by means of the ac susceptibility measurements and the singular-point-detection (SPD) technique.

II. EXPERIMENTAL DETAILS

Polycrystalline R_2Co_{17} samples with R=Y, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm were prepared by arc melting appropriate amount of raw material (of at least 99.9 wt % purity) and subsequently homogenized at 1273 K for two weeks. The homogenized samples have been checked by means of the x-ray-diffraction analysis and the standard metallurgical method. It was found that all the homogenized samples are of a single phase. No impurity phase was detected at least by the two methods mentioned above. From a careful x-ray-diffraction analysis it is deduced that R_2Co_{17} compounds with R=Y, Ce, Pr, Nd, Sm, and Gd crystallizes in the rhombohedral structure, whereas the compounds with R=Tb, Dy, Ho, Er, Tm, and Lu in the hexagonal structure. It is interesting to note that Tb_2Co_{17} and Dy_2Co_{17} are at the boundary of these two structural types. With a suitable annealing process, Dy_2Co_{17} with the rhombohedral structure was successfully obtained. Single-crystalline Pr_2Co_{17}, Nd_2Co_{17}, Tb_2Co_{17}, Dy_2Co_{17}, Ho_2Co_{17}, and Er_2Co_{17} were produced by an adapted tri-arc Czochralski technique.[21] All samples, both polycrystalline and single crystalline, have a spherical macrosymmetry with a diameter of 2–3 mm.

The temperature dependence of the ac susceptibility for all samples was measured in an ac susceptometer that can be operated from 4.2 to 300 K with the ac field from 0.4 to 800 A/m and the frequency from 5 to 1000 Hz. The measurement was performed with increasing temperature in steps of 3 degrees Kelvin. The temperature is controlled within 0.5 K in such a way that every set point needs 11 min. of measuring time. The parameters chosen for our measurements are the ac field, 40 A/m and the frequency, 1000 Hz. For the uniaxial compounds, i.e., Ce_2Co_{17}, Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17} the magnetic anisotropy field H_A was detected by the SPD technique in a pulsed-field system. This system is divided into two subsystems. One can be operated from 4.2 to 300 K with a maximum field of 300 kOe (measurements in this system were performed with decreasing temperature), whereas the other system can be operated from 300 to 1000 K with a maximum field of 280 kOe. The system is calibrated by a single-crystalline Ba ferrite (sphere) that has the anisotropy field H_A of 16.8 kOe and a saturation magnetization of 4.79 kG at 300 K [as determined by a superconducting quantum interference device (SQUID) measurement].[22]

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Spin-orientation transition and magnetic anomaly determined by measuring the temperature dependence of the ac susceptibility

Principally, the real (χ') and the imaginary (χ'') components of the ac susceptibility are obtained simultaneously when measuring the ac susceptibility. For highly anisotropic materials like R_2Co_{17}, the value of χ' of the ac susceptibility is determined mainly by the magnetic anisotropy energy and the domain-wall energy, whereas the value of χ'' of the ac susceptibility gives the energy absorption by the compound. The energy absorption comes mainly from the reversible domain-wall movement. The energy absorption due to the eddy current for these compounds is negligible. The onset temperature for the spin-reorientation transition or a magnetically anomalous phenomenon was taken to be the temperature where $d\chi'/dT$ achieves an extremum value (minimum or maximum). Furthermore, the ac susceptibility depends also on the magnetic history of the sample. In order to get the ac "initial" susceptibility—which means that the sample should be in a demagnetized state—all samples were demagnetized in an ac field prior to each measurement.

1. Y_2Co_{17}, Ce_2Co_{17}, Gd_2Co_{17}, and Lu_2Co_{17}

In the R-T intermetallic compounds, both the R sublattice and the T sublattice have contributions to the bulk anisotropy energy. The former is mainly determined by the crystalline electric field (CEF) and the R-T exchange interactions and is very strongly temperature dependent. Whereas the latter originates from noncompletely-quenched angular momentum of the 3d electrons, which, compared to the former, is less temperature dependent. The Co sublattice anisotropy can be separated by studying the isostructural R_2Co_{17} compounds where R is nonmagnetic Y or Lu or the S state Gd ions. Figure 2 shows, as an example, the temperature dependence of χ' of Ce_2Co_{17} and Gd_2Co_{17}. No anomaly can be observed in $\chi'(T)$. From these experimental results it follows that the

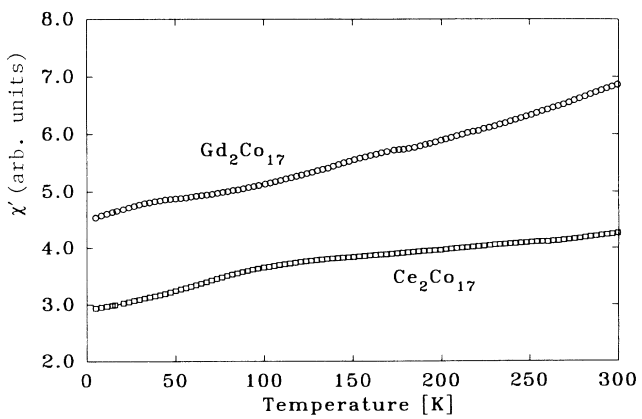

FIG. 2. Temperature dependence of the real part of the ac susceptibility, χ', of polycrystalline R_2Co_{17}. □, Ce_2Co_{17}; ○, Gd_2Co_{17}.

easy-magnetization direction (EMD) of the Co sublattice remains unchanged at least up to 900 K.[23] Therefore, the magnetic phase transition or the magnetic anomaly in R_2Co_{17}, where R is a magnetic ion with a nonzero orbit angular momentum, is caused by the change of the R sublattice anisotropy energy.

2. Pr_2Co_{17} and Nd_2Co_{17}

Figures 3 and 4 show the temperature dependence of χ' measured for polycrystalline as well as single-crystalline Pr_2Co_{17} and Nd_2Co_{17}, respectively. From these two figures, an anomaly in $\chi'(T)$ is clearly detectable at about $T_{SR}=180$ K for Pr_2Co_{17} and at about $T_{SR}=175$ K for Nd_2Co_{17}. According to the magnetization measurements performed on single crystalline Pr_2Co_{17} and Nd_2Co_{17} with the external field applied along different crystalographic directions at different temperatures from 4.2 to 250 K,[8,11] it can be concluded that this anomaly in $\chi'(T)$ is due to a spin-reorientation transition, which is characterized by a change of the EMD from the basal plane ($T > T_{SR}$) to a cone ($T < T_{SR}$). The EMD of Pr_2Co_{17} and Nd_2Co_{17} lies at 4.2 K in a cone that is, respectively, 26° and 7.6° away from the basal plane in the bc plane.[8,11] A cone spin configuration of Pr_2Co_{17} and Nd_2Co_{17} at low temperatures was also determined by Kudrevatykh *et al.*[7] The cone angle, the angle between the EMD and the basal plane, was determined at 4.2 K to be 26° and 7.5 ° for Pr_2Co_{17} and Nd_2Co_{17}, respectively, which is in fair agreement with the data obtained from the high-field measurements.[8,11] This cone spin configuration was estimated to be maintained up to 500 K.[7] However, the spin-reorientation temperatures T_{SR} determined by measuring the temperature dependence of the ac susceptibility, are lower than those obtained from the high-field magnetization measurements [>250 K (Refs. 8 and 11) and 500 K (Ref. 7)]. In principle, a spin-reorientation transition should be also detectable in the temperature dependence of χ''. This is indeed observed in Pr_2Co_{17} as can be seen in Fig. 5. Figure 6 shows the temperature dependence of χ'' of Nd_2Co_{17}. However, an anomaly at 175 K is not well visible, which might be possible due to the very small cone angle of Nd_2Co_{17} at low temperatures. Nevertheless, both Figs. 5 and 6 show a very pronounced peak at 40 K for Pr_2Co_{17} and at 70 K for Nd_2Co_{17}, which corresponds to the temperature where $\chi'(T)$ changes drastically. Two phenomena might be responsible for these peaks. First, as we have noticed in $Nd_2Fe_{14}B$, this peak in $\chi''(T)$ gives the temperature where the cone angle drastically decreases with increasing temperature.[20] This is in fact the case for Pr_2Co_{17} as confirmed in Refs. 8 and 11. Second, these peaks might be due to unfreezing of the domain-wall movement. More details about the latter will be provided later.

Since the Co sublattice anisotropy favors the basal

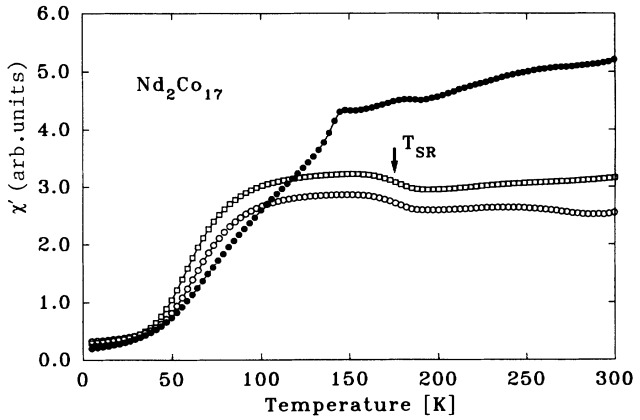

FIG. 4. Temperature dependence of the real part of the ac susceptibility, χ', of Nd_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

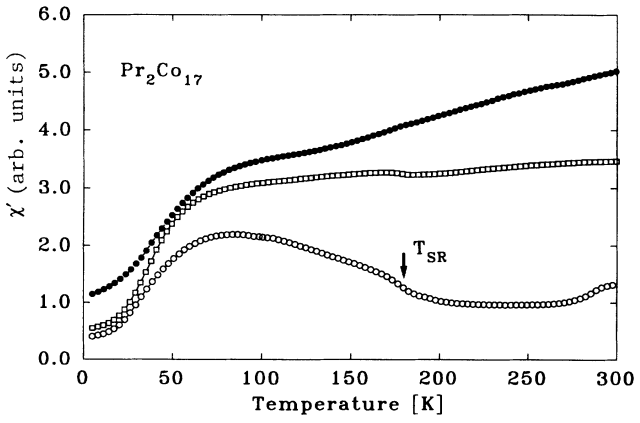

FIG. 3. Temperature dependence of the real part of the ac susceptibility, χ', of Pr_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

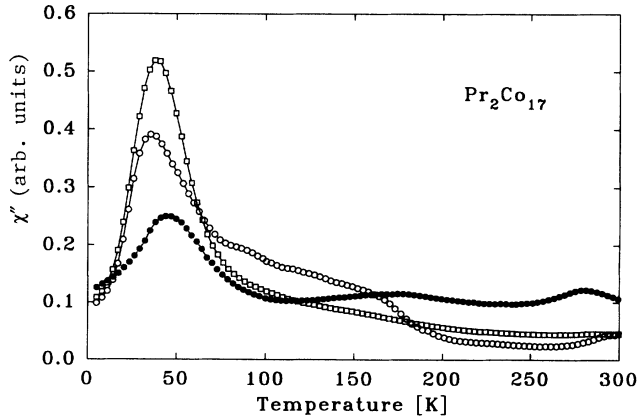

FIG. 5. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of Pr_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

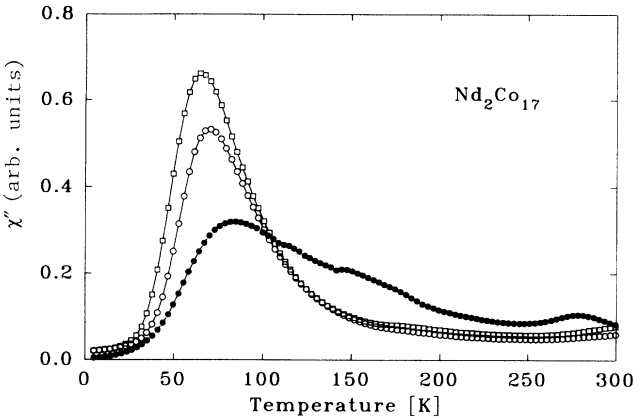

FIG. 6. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of Nd_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

plane at least below 900 K as derived from the study of Y_2Co_{17} and Lu_2Co_{17},[7,23] the cone spin configuration observed in Pr_2Co_{17} or Nd_2Co_{17} at low temperatures must be due to the crystalline electric field (CEF) experienced by Pr or Nd ions. Concerning only the rare-earth ions, the CEF Hamiltonian (taking up to fourth-order terms) of the Pr^{3+} or Nd^{3+} ion in the rhombohedral Pr_2Co_{17} or Nd_2Co_{17} can be written as

$$\mathcal{H}_{\mathrm{CEF}}=B_2^0O_2^0+B_4^0O_4^0 ,$$

where B_n^0 and O_n^0 are the CEF coefficients and the Stevens operators, respectively. It follows from the calculation that the spin-reorientation transition observed in Pr_2Co_{17} and Nd_2Co_{17} can be satisfactorily described in terms of the CEF and R-Co exchange interactions. It is known that, for both Pr^{3+} and Nd^3 ions, the second-order term $B_2^0O_2^0$ ($B_2^0>0$) has the energy minimum at $\phi=90°$ (ϕ is the angle between the EMD and the c axis) that leads to the EMD within the basal plane, meanwhile the fourth-order term $B_4^0O_4^0$ ($B_4^0>0$) has the energy minimum at $\phi=45°$, which means that the fourth-order term leads to the EMD 45° away from the basal plane. The real direction of the EMD is determined by the competition between these two terms. In the case of Pr_2Co_{17} and Nd_2Co_{17}, the contribution to the anisotropy energy from the fourth-order term overwhelms the contribution from the second-order term at low temperatures. The EMD of the compounds therefore makes an angle with the basal plane. It is worthwhile to note that the contribution to the anisotropy energy from the fourth-order term decreases much faster with increasing temperature than that from the second-order term. This gives the reason why the cone angle decreases with increasing temperature. It is also well known that the contribution to the anisotropy energy from the high-order CEF terms becomes negligible around room temperature. For this reason the cone spin configuration will become unstable well below room temperature. Therefore, it is less likely that the spin-reorientation temperatures of Pr_2Co_{17} and Nd_2Co_{17} are higher than 300 K as claimed in Ref. 7. Our preliminary calculation gives $T_{SR}=180$ K for Pr_2Co_{17} and $T_{SR}=100$ K for Nd_2Co_{17}. The less satisfactory for Nd_2Co_{17} might be due to the neglect of the sixth-order CEF terms. The cone spin configuration determined up to 250 K by the high-field magnetization measurements[8,11] might be due to a small misalignment of the single crystal. It is therefore more reliable to accept the spin-reorientation temperature determined by the ac susceptibility measurement, i.e., 180 K for Pr_2Co_{17} and 175 K for Nd_2Co_{17}, respectively. These data are shown in Fig. 1.

3. Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17}

The temperature dependence of χ' measured for polycrystalline as well as single crystalline Tb_2Co_{17} is shown in Fig. 7. From Fig. 7, at least two aspects can be clearly noticed. First, an anomaly in $\chi'(T)$ is evident at about 170 K; second, this anomaly depends upon the crystallographic directions. The anomaly becomes more pronounced when the external field is applied within the basal plane (perpendicular to the c axis). This fact—similar to the case, as we shall mention later, of the other compounds—indicates that this anomaly observed in $\chi'(T)$ as well as in $\chi''(T)$ is an intrinsic property of Tb_2Co_{17} and not due to an impurity phase. This anomaly becomes even more evident in the temperature dependence of χ'' as can be seen in Fig. 8. Furthermore, it follows from Fig. 8 that the energy absorption of Tb_2Co_{17} decreases with increasing temperature and becomes nearly zero at around 170 K where $\chi'(T)$ shows an anomaly. This nonzero χ'' of Tb_2Co_{17} indicates also that domain wall is excited to move by the external ac field from 4.2 to around 170 K. This fact will be discussed in detail later. In order to get information about the effects of the external field and the frequency on the ac susceptibility, we have performed measurements of the temperature dependence of the ac susceptibility on Tb_2Co_{17} single crystal at

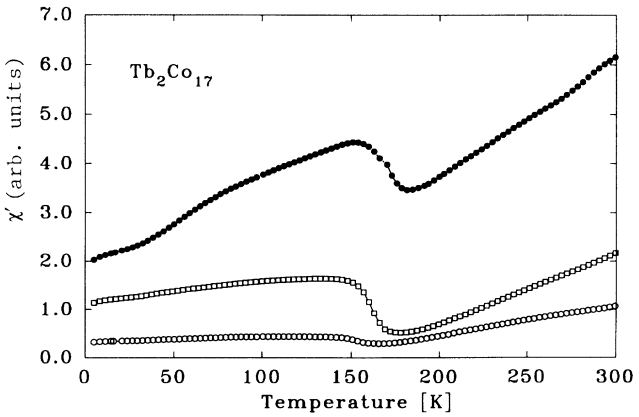

FIG. 7. Temperature dependence of the real part of the ac susceptibility, χ', of Tb_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

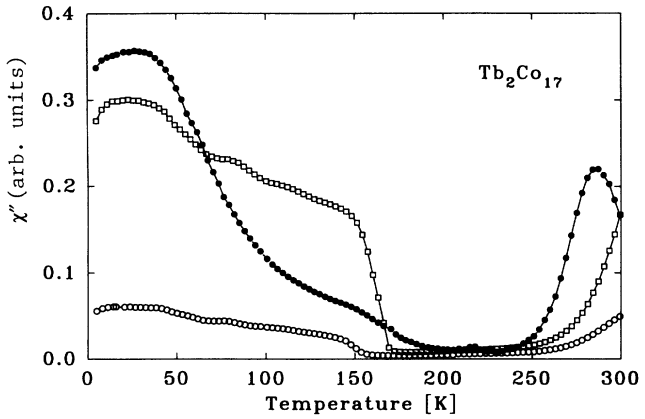

FIG. 8. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of Tb_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

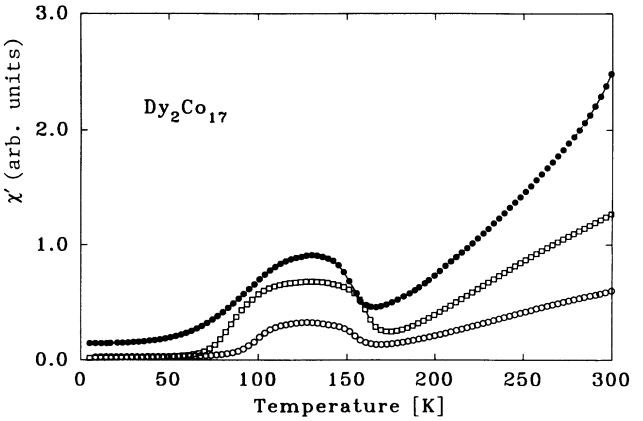

FIG. 10. Temperature dependence of the real part of the ac susceptibility, χ', of Dy_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis and the basal plane; □, single crystal, measured with the external ac field applied perpendicular to the c axis.

different frequency from 5 to 1000 Hz and different magnitudes of the external field from 1 to 800 A/m. Figure 9 shows the thus obtained results. It is evident from this figure that the absolute value of ac susceptibility can be influenced both by the frequency and by the external field. However, the onset temperature of the anomaly remains unchanged varying the frequency from 5 to 1000 Hz, whereas the onset temperature increases with increasing external ac field.

Anomalous phenomena, as found in Tb_2Co_{17}, have also been observed for Dy_2Co_{17} and Ho_2Co_{17}. Figures 10 and 11 show, as an example, the temperature dependence of χ' and χ'' of polycrystalline as well as single-crystalline Dy_2Co_{17}. The values of χ' and χ'' at 4.2 K of Dy_2Co_{17} are much lower than these of Tb_2Co_{17} as can be seen in Figs. 10 and 11 (compared to Figs. 7 and 8, respectively).

It is evident from Figs. 10 and 11 that an anomaly at the temperature range 69–162 K appears in $\chi'(T)$. Contrary to Tb_2Co_{17}, the anomaly found in Dy_2Co_{17} exists in a broad temperature range rather than a peaklike transition in Tb_2Co_{17}. The temperature dependence of χ'' of Dy_2Co_{17} demonstrates a very different temperature behavior as observed in Tb_2Co_{17} (see Fig. 11). The values of χ'' remain very low in the temperature range from 4.2 to about 70 K, increase very dramatically to a maximum at about 90 K, decrease again to the same values as in 4.2 K at 162 K, remain these values till about 250 K, and then increase continuously. Again the dependence of this anomaly on the crystallographic directions can be clearly seen from Figs. 10 and 11. As we have mentioned in previous section, Dy_2Co_{17} with the rhombohedral structure has been successfully obtained under the suitable anneal-

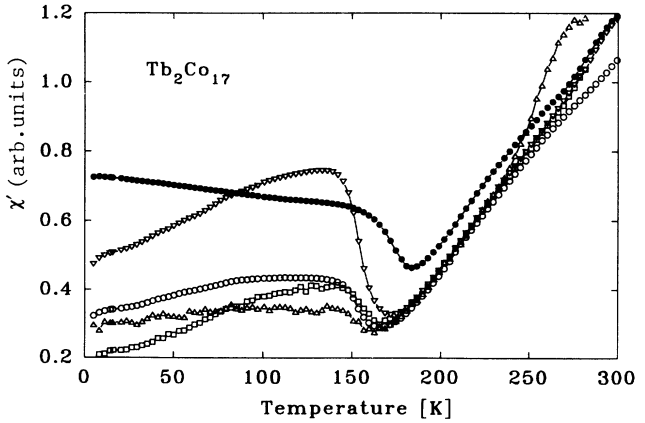

FIG. 9. Temperature dependence of the real part of the ac susceptibility, χ', of single-crystalline Tb_2Co_{17} under the different frequency and the different amplitudes of the external ac field applied to the direction between the c axis and the basal plane. □, (125 Hz, 1 A/m); △, (5 Hz, 40 A/m); ○, (125 Hz, 40 A/m); ▽, (1000 Hz, 40 A/m); ●, (125 Hz, 800 A/m).

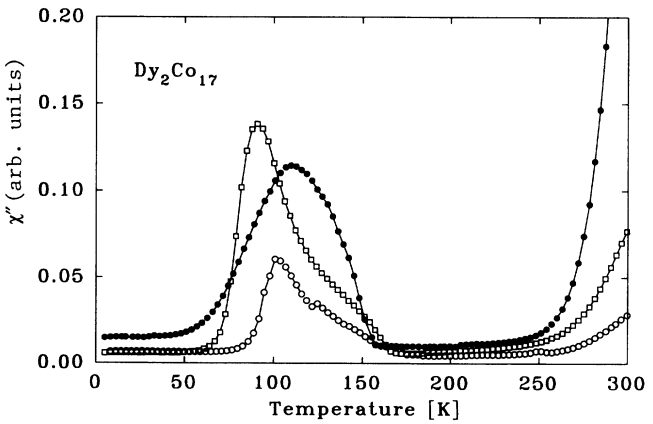

FIG. 11. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of Dy_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the external ac field applied to the direction between the c axis, and the basal plane; □, measured for the single crystal with the external ac field applied perpendicular to the c axis.

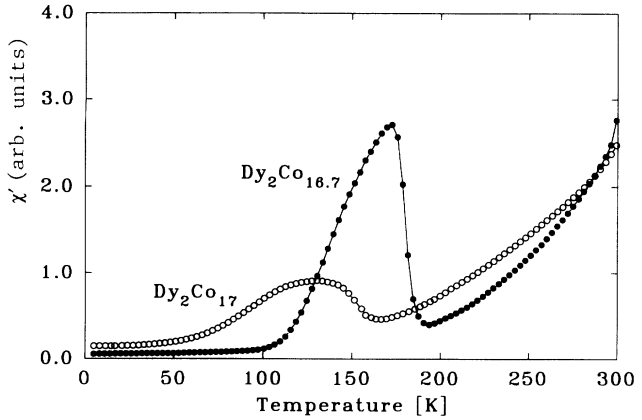

FIG. 12. Temperature dependence of the real part of the ac susceptibility, χ', of polycrystal rhombohedral $Dy_2Co_{16.7}$ (●) and hexagonal Dy_2Co_{17} (○).

ing process with slightly changing the composition ($Dy_2Co_{16.7}$). Figures 12 and 13 show the temperature dependence of χ' and χ'' for rhombohedral $Dy_2Co_{16.7}$. The results of hexagonal Dy_2Co_{17} are included for comparison. Similar as in hexagonal Dy_2Co_{17}, a very pronounced anomaly was detected at the temperature range 94–187 K, which is higher than from 69 to 162 K as observed in hexagonal Dy_2Co_{17}.

From the high-field magnetization measurements on Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17} at 4.2 K (Refs. 8, 17, 18, and 24) and at temperatures from 4.2 to 900 K,[4,7] there is no evidence for a change of the EMD. Unlike the case of Pr_2Co_{17} and Nd_2Co_{17}, this anomaly in $\chi'(T)$ and $\chi''(T)$ of Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17} is, therefore, not due to a spin-reorientation transition. We have also noticed that an anomaly in the temperature dependence of the anisotropy constant K ($K=K_1+2K_2+\ldots$) was also found at about the same temperature range where an anomaly appears in $\chi'(T)$ and $\chi''(T)$ for Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17} by Kudrevatykh *et al.*[7] and Deryagin and coworkers.[4,5]

In order to trace the physical nature of this anomaly observed in Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17}, the measurement of the temperature dependence of the magnetization was performed on single-crystalline Dy_2Co_{17} with the external field of 10 kOe applied in different crystallographic directions. Figure 14 shows the thus measured result. It follows from this figure that the magnetization measured along the a axis and the b axis becomes identical above 170 K, the temperature where $\chi'(T)$ and $\chi''(T)$ show an anomaly, which implies that above this temperature the basal-plane anisotropy energy become very small. This fact suggests that the anomaly in $\chi'(T)$ and $\chi''(T)$ observed in Dy_2Co_{17} is correlated with the disappearance of the anisotropy energy within the basal plane.

To analyze the complex ac magnetic initial susceptibility is not an easy task. Recently, Rillo *et al.*[25] calculated the ac susceptibility of single-crystalline $Ho_2Fe_{14}B$, which has the 180° domain wall above the spin-reorientation temperature. Two main contributions, the coherent rotation of the magnetic moment and reversible domain-wall movement excited by the ac field, to the ac susceptibilityy were analyzed in their calculation. It was proposed that the domain-wall movement gives the main contribution to the ac susceptibility when the external ac field is applied parallel to the c axis. A nonzero χ'' is direct evidence for domain-wall movement, especially in the case when the external field is applied parallel to the c axis. For R_2Co_{17} compounds with basal-plane anisotropy like Tb_2Co_{17} and Dy_2Co_{17}, the domain structure is unknown. However, by considering the characteristics of the magnetic anisotropy, it can be predicted that these compounds hold a 60° domain wall. The effective domain-wall width (δ) is proportional to $(K_A)^{-1/2}$, where K_A is the anisotropy constant.[26] If the anisotropy is very large, the domain wall becomes a narrow wall which is difficult to move under excitation by the external ac field. On the other hand, if the anisotropy is very small, the domain wall becomes so wide that it can be pinned by the sample surface (for single crystal) or a grain boundary (for polycrystals). Such a wide domain wall is also difficult to move under excitation by the external ac field. Therefore, only medium-size domain walls give contributions to the ac susceptibility. Since the anisotropy energy (K_A)

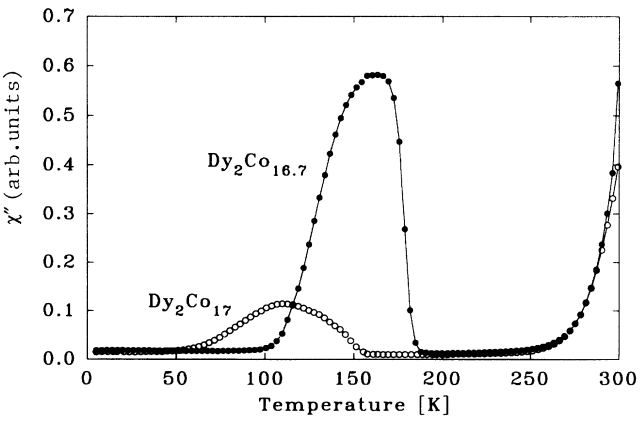

FIG. 13. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of polycrystal rhombohedral $Dy_2Co_{16.7}$ (●) and hexagonal Dy_2Co_{17} (○).

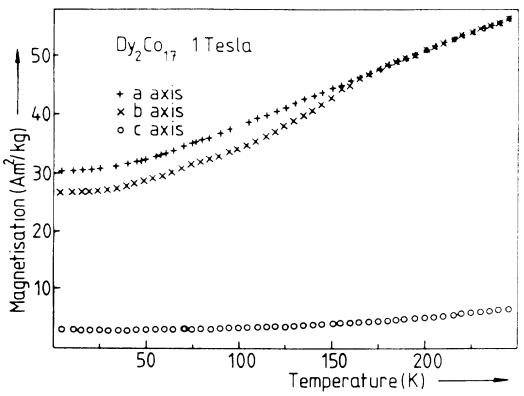

FIG. 14. Temperature dependence of the magnetization measured on the single-crystalline Dy_2Co_{17} with the external field of 10 kOe applied in different crystallographic directions [after Sinnema (Ref. 8)].

decreases with increasing temperature, the domain-wall width will change with varying temperature. Therefore, the temperature-induced change of the domain-wall structure can be detected by measuring the temperature dependence of the ac susceptibility. According to the above general discussion, the following explanation can be drawn for Tb_2Co_{17} and Dy_2Co_{17}: The large values of χ' and χ'' of Tb_2Co_{17} (see Figs. 7 and 8) at low temperatures suggest that the anisotropy within the basal plane of Tb_2Co_{17} is small. The domain-wall movement is not frozen and makes the main contribution to the ac susceptibility. In particular, the fact that the values of χ' and χ'' measured with the external field applied within the basal plane are larger than those measured with the external field applied along other directions is direct evidence in support of the above conclusion. A continuous decrease of χ'' with increasing temperature suggests that domain-wall movement becomes increasingly difficult with increasing temperature. Above 170 K (say pinning temperature), χ'' decreases dramatically to a very low value. This fact implies that above that temperature the domain wall is pinned. The domain wall cannot move under excitation by the external ac field, therefore making no contribution to the ac susceptibility. For a larger amplitude of the external field, the pinning temperature will increase. This is in fact observed as can be seen in Fig. 9. For Dy_2Co_{17}, the values of χ' and χ'', in temperature range from 4.2 to about 70 K, are much lower than that for Tb_2Co_{17} (see Figs. 10 and 11 and compare to Figs. 7 and 8, respectively). This fact suggests that in this temperature range the domain wall is completely frozen, which is due to the large anisotropy within the basal plane of Dy_2Co_{17} and, consequently, the narrow domain wall. In fact, the anisotropy energy E_A within the basal plane of R ion at $T=0$ K in R_2Co_{17} can be calculated from the expression

$$E_A = B_6^6 J(J-1/2)(J-1)(J-3/2)(J-2)(J-5/2) ,$$

where B_6^6 is the sixth-order CEF coefficient and J is the total angular momentum. From this calculation, it is deduced that the value of E_A(Dy) is 4.4 times larger than that of E_A(Tb). In the temperature range from about 70 to 160 K, a dramatic change and also the large values of χ' and χ'' imply that the domain-wall movement is unfrozen, which is due to the change of the anisotropy energy and in turn the domain-wall width. Above 160 K the basal-plane anisotropy energy becomes very small (see also Fig. 14). The domain-wall width will be expanded dramatically. Above this temperature, the domain wall is proposed to be pinned by the sample surface (for single crystals) or a grain boundary (for polycrystals).

4. Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17}

For all these three compounds, the EMD is along the c axis. A 180° domain wall is predicted. Figures 15 and 16 show the temperature dependence of χ' and χ'' of Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17}. Due to the large uniaxial anisotropy (see Fig. 20) at low temperatures, the domain-wall width of these compounds will be very narrow and, consequently, the domain wall is difficult to move under excitation by the external ac field. This is in fact confirmed by the very low χ' values of these three compounds at the temperature range below about 100 K. The values of χ' and χ'' of Sm_2Co_{17} remains very low up to 300 K. This fact can be understood in view of the very large uniaxial anisotropy (see Fig. 20) of Sm_2Co_{17} in this temperature range, and consequently, the narrow domain wall. In order to find a reason for the increase of χ' and χ'' of Er_2Co_{17} and Tm_2Co_{17} above about 100 K, an ac susceptibility measurement was performed on the single-crystalline Er_2Co_{17}. Figures 17 and 18 show the temperature dependence of χ' and χ'' of polycrystalline as well as single-crystalline Er_2Co_{17}. Very low values of χ' and χ'' are found for single-crystalline Er_2Co_{17} when the external field is applied perpendicular to the c axis, in which case the contribution to the ac susceptibility is mainly due to a coherent rotation of the magnetic moment. This fact gives direct evidence that the contribution to the ac susceptibility from the coherent rotation of the magnetic moment are very small. Again a drastic change of χ' and χ'' is found for single-crystalline Er_2Co_{17} with the exter-

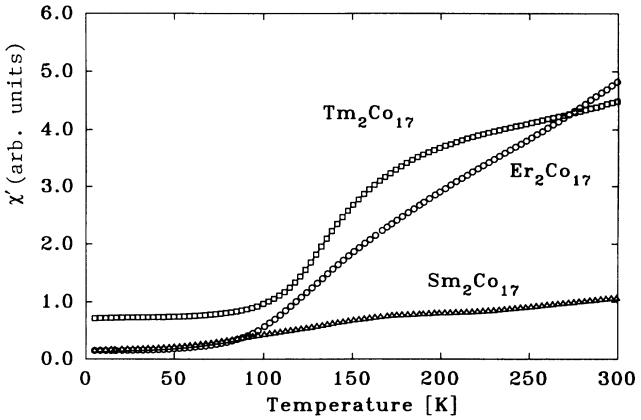

FIG. 15. Temperature dependence of the real part of the ac susceptibility, χ', of polycrystalline R_2Co_{17}. △, Sm_2Co_{17}; ○, Er_2Co_{17}; □, Tm_2Co_{17}.

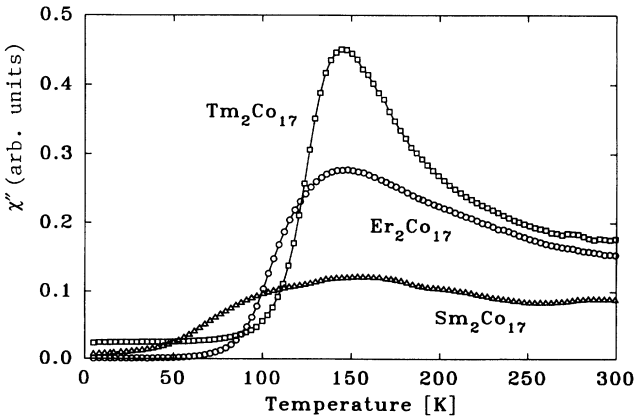

FIG. 16. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of polycrystalline R_2Co_{17}. △, Sm_2Co_{17}; ○, Er_2Co_{17}; □, Tm_2Co_{17}.

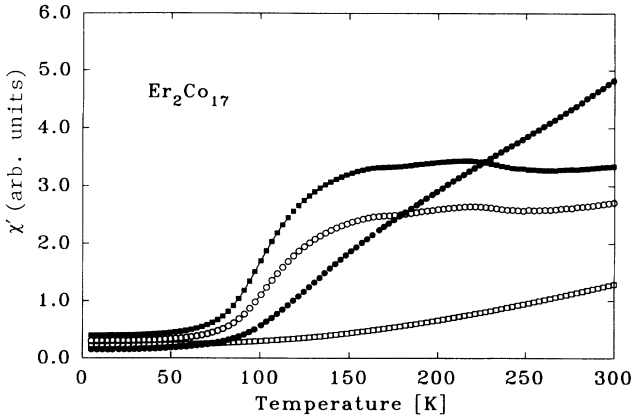

FIG. 17. Temperature dependence of the real part of the ac susceptibility, χ', of Er_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the field applied in the direction between the c axis and the basal plane; ■, single crystal, measured with the field applied parallel to the c axis; □, single crystal, measured with the field applied perpendicular to the c axis.

nal ac field applied parallel to the c axis. Therefore, it can be concluded that the drastic changes of χ' and χ'' for Er_2Co_{17} and Tm_2Co_{17} above 100 K are due to an unfreezing of the domain-wall movement, which is initiated by a drastic decrease of the anisotropy (see Fig. 20).

B. The magnetocrystalline anisotropy field determined by the singular point detection technique

The anisotropy field H_A as well as its temperature dependence is an important parameter to characterize hard magnetic materials. The value of the anisotropy field gives the upper limit of the realized coercive force for permanent magnets. Therefore, the determination of the magnetic anisotropy field becomes an extremely important task in the research of hard magnetic materials. Experimentally, the anisotropy field can be determined either on the single-crystalline samples or in the magnetically oriented samples by the Sucksmith-Thompson method.[27] However, because of the difficulties in producing single crystals, the application of the former method is very limit, whereas the latter method always gives an overestimated value of H_A.[28] A method for directly determining H_A by the measurement on the polycrystalline samples is therefore considered highly desirable. Fortunately, it has been predicted by Asti and co-workers that, for compounds with an uniaxial anisotropy, the anisotropy field H_A can be detected by a singularity in the curve of d^2M/dH^2 versus the applied field H.[29–31] This idea is nowadays recognized as the singular-point-detection (SPD) theory and has recently become a very useful tool to directly determine the anisotropy field of uniaxial R-T compounds in a polycrystalline state. As mentioned above, this SPD peak can only be detected for compounds that have an EMD parallel to the c axis. Therefore this method can also be used to determine the EMD of the compounds. In the present investigation this unique method has been used to determine the anisotropy field of uniaxialy anisotropic Ce_2Co_{17}, Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17}.

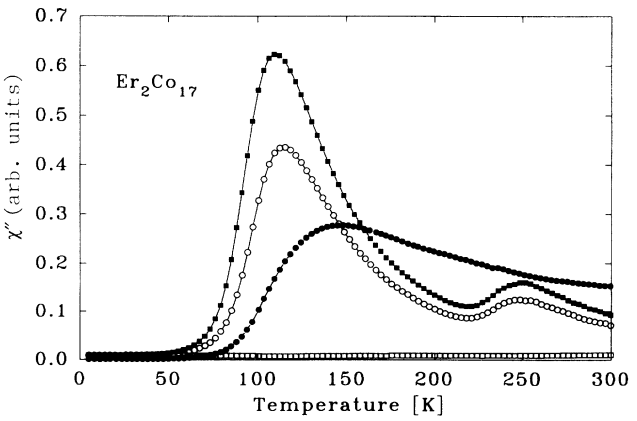

FIG. 18. Temperature dependence of the imaginary part of the ac susceptibility, χ'', of Er_2Co_{17}. ●, polycrystal; ○, single crystal, measured with the field applied in the direction between the c axis and the basal plane; ■, single crystal, measured with the field applied parallel to the c axis; □, single crystal, measured with the field applied perpendicular to the c axis.

1. *Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17}*

Figure 19 shows the singularity that indicates the anisotropy field in d^2M/dH^2 versus H curve for Er_2Co_{17} measured at 300 K. As can be seen in Fig. 19, a well resolved peak at $H=H_A$ can be detected. Figure 20 shows the temperature dependence of H_A determined by the SPD technique for Ce_2Co_{17}, Sm_2Co_{17}, Er_2Co_{17}, and Tm_2Co_{17} at various temperatures from 4.2 to 1000 K. From Fig. 20 it is evident that the anisotropy field of Sm_2Co_{17} is much larger than that of Er_2Co_{17} and Tm_2Co_{17} in the temperature range from 100 to 1000 K. The value of H_A for Sm_2Co_{17} is 71 kOe at room temperature, which is slightly smaller than that of the well-known $Nd_2Fe_{14}B$ [$H_A=82$ kOe at 300 K (Ref. 20)]. However, at 550 K the anisotropy field of Sm_2Co_{17} is still 27 kOe, whereas that of $Nd_2Fe_{14}B$ is only 13 kOe.[20] This

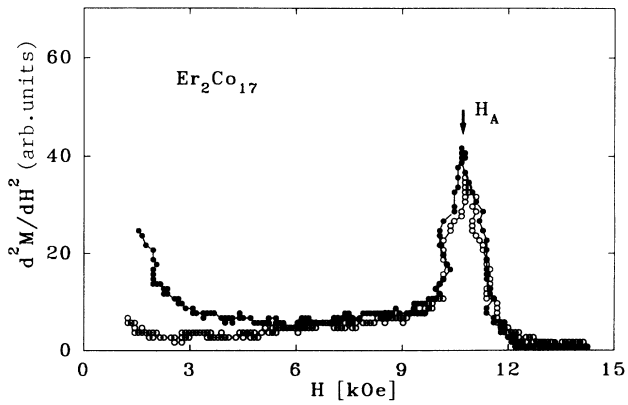

FIG. 19. The singularity in the curve of d^2M/dH^2 vs H of polycrystalline Er_2Co_{17} at 300 K. ●, measured with increasing the continuously pulsed field; ○, measured with decreasing the continuously pulsed field.

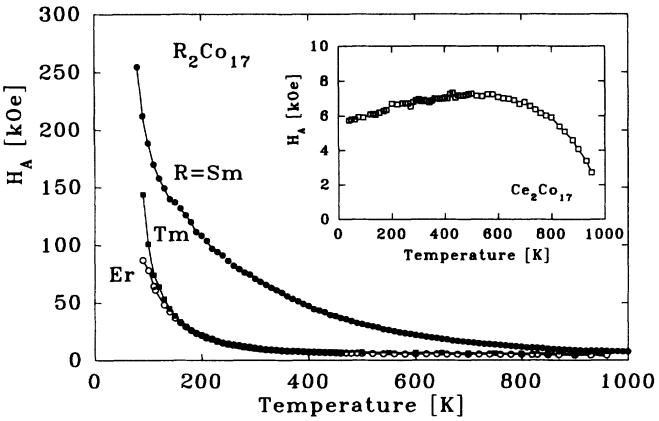

FIG. 20. Temperature dependence of the anisotropy field H_A of Sm_2Co_{17} (●), Er_2Co_{17} (○), Tm_2Co_{17} (■), and Ce_2Co_{17} (□).

is the intrinsic reason why the coercivity of Sm_2Co_{17} is thermally much more stable than $Nd_2Fe_{14}B$. For Er_2Co_{17}, Chen *et al.*[23] claimed a spin-reorientation transition at about 800 K. However, we detected a SPD peak for Er_2Co_{17} till 950 K, which implies that at least till 950 K the EMD of Er_2Co_{17} is along the c axis. The absence of a spin-reorientation transition, from the c axis to the basal plane with increasing temperature, in Er_2Co_{17} can also be understood by the spin-reorientation transition, from the basal plane to the c axis, observed in Y_2Co_{17} ($T_{SR}=1040$ K) and Gd_2Co_{17} ($T_{SR}=950$ K) by the same authors[23] (see Fig. 1).

2. Ce_2Co_{17}

Among all rare-earth–transition-metal intermetallic compounds, Ce compounds stands out as being anomalous in several respects. First, there are clear anomalies in the lattice constants for $CeCo_5$,[32] Ce_2Co_{17},[33] Ce_2Fe_{17},[34] and $Ce_2Fe_{14}B$,[35] with respect to other isostructural compounds as shown for an example for R_2Co_{17} in Fig. 21. Second, the magnetic properties, as for example reflected in the Curie temperature (see Fig. 1), deviate significantly from the values obtained from a simple extrapolation by the other R_2Co_{17} compounds. The magnetic moment of Ce compounds is anomalously low when compared to Y and Lu compounds.[6,7] These anomalies have been interpreted as evidence for a mixed-valence behavior of the cerium ion; the effective occupation number of the $4f$ shell is somewhere between zero and one. However, it is well-accepted to treat Ce ions in R-T compounds as nonmagnetic element. Considering the magnetic anisotropy, Ce compounds are usually considered to behave similarly as the isostructural Y, La, Gd, or Lu compound. This is in fact also valid for RCo_5 (Ref. 36), R_2Fe_{17} (Ref. 34), and $R_2Fe_{14}B$ (Refs. 35 and 37) compounds. However, in R_2Co_{17} compounds this commonly used idea is no longer valid. As we mentioned previously, the anisotropy of the Co sublattice in R_2Co_{17}, as derived from studying of Y_2Co_{17}, Gd_2Co_{17}, and Lu_2Co_{17}, favors the basal plane in the temperature range below at least 900 K.[23] On the other hand, the anisotropy of Ce_2Co_{17} favors the c axis in the whole magnetically ordered temperature range as verified in Fig. 20 (inset of figure) and Fig. 22. The values of H_A of Ce_2Co_{17} increase with increasing temperature from 4.2 K, and reach a maximum at about 500 K before dropping to zero at the Curie temperature. The uniaxial anisotropy of Ce_2Co_{17} was also confirmed by the measurement on the single-crystalline Ce_2Co_{17}.[7] Additionally, we have noticed that, in RCo_5 (Ref. 36) and $R_2Fe_{14}B$ (Refs. 35 and 37) compounds, the anisotropy energy of Ce compounds are also anomalously larger than that of the isostructral Y, La or Lu compound. Recently, Nordström *et al.*[32] calculated the electronic structure of $CeCo_5$. It is shown from this calculation that the anomalous properties of $CeCo_5$ are due to an itinerant $4f$ state. The hybridization of the cerium $4f$ states and the cobalt $3d$ states is the reason of the itinerant $4f$ state. Similarly as in $CeCo_5$, the hybridization of the cerium $4f$ states and the cobalt $3d$ states will play an important role in determining the magnetic properties of Ce_2Co_{17}. This hybridization is the actual reason of the anomalous properties of Ce_2Co_{17}. From the uniaxial anisotropy of Ce_2Co_{17} observed in the present investi-

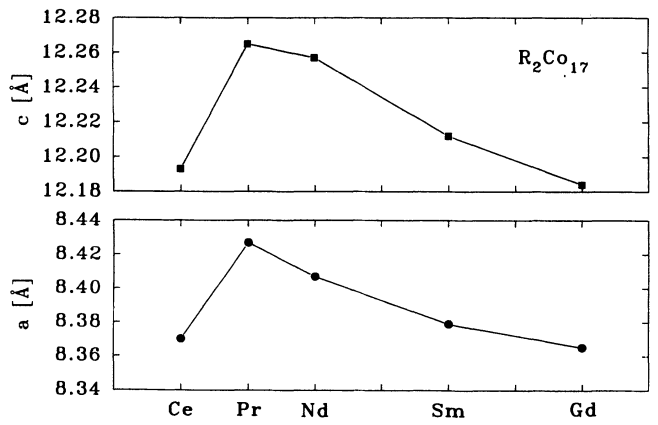

FIG. 21. Lattice constants, a and c, of the rhombohedral R_2Co_{17}.

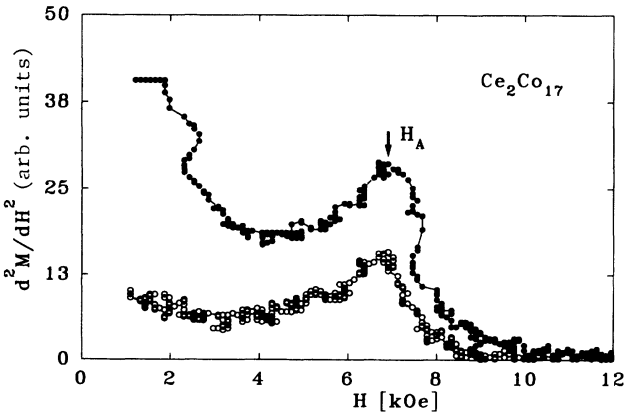

FIG. 22. The singularity in the curve of d^2M/dH^2 vs H of polycrystalline Ce_2Co_{17} at 300 K. ●, measured with increasing the continuously pulsed field; ○, measured with decreasing the continuously pulsed field.

gation, it follows that the contribution to the bulk anisotropy from the Ce ions of Ce_2Co_{17} is nonzero, but uniaxial. It means that in Ce_2Co_{17}, the uniaxial Ce-sublattice anisotropy dominates the relatively weak planar Co-sublattice anisotropy over the whole magnetically ordered temperature range.

IV. CONCLUSION

In this paper, we have reported a systematic study on a whole series of R_2Co_{17} compounds by means of the ac susceptibility and the magnetic anisotropy field measurements. A spin-reorientation transition was found in Pr_2Co_{17} and Nd_2Co_{17}, and the spin-reorientation temperature T_{SR} was precisely determined. A magnetic anomalous phenomenon, which is characterized by a peaklike change in the curve of $\chi'(T)$ and $\chi''(T)$, was observed in Tb_2Co_{17}, Dy_2Co_{17}, and Ho_2Co_{17}, of which the EMD lies within the basal plane. From the temperature dependence of the magnetization measurement performed on Dy_2Co_{17} single crystal, with the external field (10 kOe) applied along different crystallographic directions, it follows that the physical nature of this magnetic anomalous phenomenon is correlated with the disappearance of the magnetic anisotropy energy within the basal plane. For uniaxial anisotropy Er_2Co_{17} and Tm_2Co_{17} compounds, a dramatical change, rather than a peaklike anomaly, occurs at the temperature above about 100 K. This temperature behavior is in fair concord with the dramatic decrease of the magnetic anisotropy field of Er_2Co_{17} and Tm_2Co_{17} around 100 K as determined by the SPD technique. By measuring the temperature dependence of the ac susceptibility on single-crystalline Er_2Co_{17} with the external ac field applied along different crystallographic directions, it is deduced that the anomalous change of $\chi'(T)$ and $\chi''(T)$ of Er_2Co_{17} and Tm_2Co_{17} is due to an ac field-induced domain-wall movement. In order to explain the ac susceptibility anomaly found in R_2Co_{17}, a model, however qualitative, is proposed based on the assumption that domain-wall movement can be either frozen because of the narrow wall (resulting from high magnetic anisotropy) or be stopped by the domain-wall pinning by a grain boundary (in polycrystals) or the sample surface (for single crystals). The EMD of Ce_2Co_{17} is found to be along the c axis over the whole magnetically ordered temperature. We have been able to measure the uniaxial anisotropy field of Sm_2Co_{17} in the temperature range from 4.2 to 1000 K.

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