Spectrum of higher harmonics of the magnetization near T_C in $CdCr_2S_4$

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An investigation is reported of the nonlinear susceptibility of ferromagnetic $CdCr_2S_4$ in the vicinity of the Curie point T_C. The experiments were carried out at frequencies up to 10^5 Hz in a wide range of amplitudes of an oscillatory magnetic field. The temperature dependence of the critical field, below which the field could be regarded as weak and above as strong, was determined. An analysis of the harmonic spectra indicated that above T_C a large fraction of the field energy was transferred to higher harmonics; a slow fall of the amplitudes of the harmonics on increase in their number (frequency) was observed. The temperature dependence of the amplitudes of higher harmonics was obtained in a strong field.

Earlier, we investigated the critical behavior of the linear and nonlinear components of the magnetic susceptibility of weakly anisotropic ferromagnets of the $CdCr_2S_4$ type earlier using rf methods[1,2]; we concluded that there were two temperature regions—scaling and anomalous—above the Curie point. The scaling or normal region, corresponding to relatively low values of the static susceptibility ($4\pi\chi_0 < 25$) for $\tau > 1\times 10^{-2}$ [$\tau = (T - T_C)/T_C$], is characterized by a satisfactory agreement of the experimentally determined behavior of the linear and nonlinear susceptibilities with the theory of static and dynamic scaling. However, the results obtained in the anomalous region ($4\pi\chi_0 > 25$) adjoining directly the Curie point T_C, disagree very strongly with the scaling theory predictions.

We consider in some detail phenomena typical of the anomalous temperature region. It follows from the results of Ref. 1 that in this region the real part of the susceptibility (χ') (measured at frequencies below 10^5 Hz) rises logarithmically when the frequency is lowered, whereas the imaginary part (χ'') depends weakly on the frequency ω. Consequently, in the lf range (10^2–10^5 Hz) the experimental values of χ' and χ'' are related by the $2/\pi$ rule[1] (to within 30%):

$$\chi'(\omega) = \frac{2}{\pi}\chi'' \ln\frac{\Omega_0}{\omega} \tag{1}$$

(Ω_0 is a characteristic frequency which depends only on temperature), which follows from the Kramers–Kronig relationships. This behavior of the frequency dependences $\chi'(\omega)$ and $\chi''(\omega)$ demonstrates the presence of a wide range of relaxation times, as is true, for example, of spin glasses.[3] Slow relaxation is related also to the appearance, above T_C, of a residual (remnant) magnetization observed in experiments on the second harmonic of an emf induced in a measuring coil.[2] These experiments revealed that, after a sample is cooled in a static magnetic field, the second harmonic measured above T_C remains finite when this field is switched off (it follows from symmetry considerations that the second harmonic of the magnetization should vanish in the paramagnetic phase in the absence of a static magnetic field). However, we have been unable to identify the nature of the relaxation of the residual magnetization, since even at relatively low amplitudes of the oscillatory magnetic field the behavior of the residual second-harmonic signal is complicated by the appearance of random oscillations (for details see Ref. 4).

A wide spectrum of the relaxation times, with an upper limit much higher than the real times found by observation, and the consequent residual magnetization are typical characteristics of the spin glass state. It follows from the above account that similar effects are observed near T_C also in ferromagnets of the $CdCr_2S_4$ type. This suggests that the anomalous temperature region represents the spin glass state. The physical reason for the appearance of the spin glass characteristics in the critical region is clearly associated with the unavoidable presence of defects or impurities in real crystals, which can give rise to random frustrations as a result of the competing ferromagnetic and antiferromagnetic interactions typical of these ferromagnets. (Single crystals of $CdCr_2Se_4$ and $CdCr_2S_4$ investigated by us earlier[1,2] were grown at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences and at the Institute of Applied Physics of the Academy of Sciences of the Moldavian SSR, and their compositions were close to stoichiometric. However, no analysis of microimpurities was made.)

The theory predicts[5] an increase in the amplitudes of the higher harmonics of the magnetization of a ferromagnet as the temperature approaches T_C. This behavior has been observed experimentally in the scaling region.[2] The question naturally arises as to the behavior of higher harmonics in the anomalous (spin-glass-like) temperature region. This question is especially important because, to the best of our knowledge the higher harmonics (with the exception of the third) have not yet been investigated for ordinary spin glasses.

We shall report the results of an investigation of the behavior of higher harmonics in the anomalous region. Our experiments were carried out on a single crystal of $CdCr_2S_4$ ($T_C \approx 84$ K) in the absence of a static magnetic field, so that the investigated spectrum contained only the odd harmonics. The even harmonics due to the influence of the residual (after screening) geomagnetic field (≈ 20 mOe) were observed only in the immediate vicinity of T_C. However, their amplitude was low compared with the amplitudes of the adjoining odd harmonics and in our analysis we ignored the even harmonics.

In an investigation of the nonlinear susceptibility we should remember that the demagnetization effects associated with the shape of a sample can suppress strongly the higher harmonics. This was considered on the basis of the scaling

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theory in Ref. 5, where the following expression was obtained:

$$m_{2n+1}(t)=M(\tau)\left(\frac{g\mu h_e}{\Omega_e}\right)^{2n+1}\frac{r_{2n+1}}{1+4\pi\chi_0 N}\cos(2n+1)\omega t, \quad (2a)$$

$$h_e=h_0/(1+4\pi\chi'(\omega)N). \quad (2b)$$

Here, $M(\tau) = M_0\tau^{\beta}$, where $\beta\approx 1/3$ and M_0 is a quantity of order of the spontaneous magnetic moment at $T=0$; $\Omega_e = kT_c\tau^{5/3}$ is an energy of the same order as the characteristic exchange energy in the dynamic scaling theory; r_{2n+1} is the nondimensional amplitude independent of τ; g is the g factor; μ is the Bohr magneton.

A characteristic feature of the above expression is that the whole dependence on the shape of the sample, i.e., on the demagnetization factor N, is included in Eq. (2b) which describes the replacement of an external field h_0 with an internal field h_e; it also occurs in the additional factor $(1+4\pi\chi_0 N)^{-1}$. The other factors in Eq. (2a) are independent of N. The relationship between m_{2n+1} and N applies irrespective of the actual theory describing the magnetic system. This follows directly from the method used to derive Eq. (2a), given in Ref. 5. It is clear from Eq. (2a) that if we have $N\neq 0$ and $4\pi\chi>1$, the reduction in the higher harmonics when n increases is enhanced as a result of demagnetization. Therefore, in order to avoid the influence of these effects on the behavior of the higher harmonics, we selected a ring-shaped sample (characterized by $N=0$ and, consequently, by $h_e = h_0$). A toroidal coil was wound uniformly on this sample: this coil was used both to create an oscillatory magnetic field $h = h_0 \sin 2\pi f_0 t$ inside the sample and also as a measuring sensor. The emf generated in this coil was applied to a spectrum analyzer with a sensitivity of ≈ 0.1

Selection of the frequency range was determined primarily by the available information[1,2] on the behavior of the linear dynamic susceptibility at frequencies 10^2–10^5 Hz. The fundamental frequency was selected to ensure that the maximum number of harmonics (for a given sensitivity of the apparatus) was available for amplitude analysis in the selected range. Since the upper limit to the range was 100 kHz, we were able to analyze no more that thirty odd components of the spectrum (when the fundamental frequency was $f_0 = 1.6$ kHz). In some cases the behavior of the higher harmonics was investigated also at other frequencies. Overloading of the input amplifier was avoided by placing a rejection filter at its input in order to attenuate the fundamental-frequency signal by a factor of about 10^3.

The maximum amplitude of the oscillatory field available in these experiments was less than 3 Oe. The following comments should be made about the field intensity. In studies of critical phenomena it is usual to distinguish weak and strong fields. It follows from the scaling theory (see, for example, Ref. 5) that in the case of isotropic ferromagnets, which include our sample because of the weak cubic anisotropy, a field is weak if it obeys the condition $g\mu h \ll kT_C\tau^{5/3}$. Naturally, the scaling ideas cannot be applied to the anomalous temperature range characterized by slow relaxation. However, control experiments carried out in fields which were weak in accordance with the scaling criterion indicated that the position of the maximum of the temperature dependence of the higher harmonics was independent of the value of h_0 and ω_0 (at least at frequencies below 10^5 Hz). On the other hand, when the field amplitude exceeded even slightly the critical values set by the scaling theory and given by $g\mu h_{cr} = k\tau_C\tau^{5/3}$, it was found that the maximum of the dependence $A_{2n+1}(T)$ shifted toward lower temperatures.

The scaling condition of field weakness is fairly stringent; for example, for $\tau = 1\times 10^{-2}$, then $h_{cr}\approx 200$ Oe, whereas for $\tau = 1\times 10^{-4}$ the critical field does not exceed 0.1 Oe. Therefore, it follows from the scaling theory that in investigations carried out in a wide temperature range an oscillatory field with the maximum (in our experiments) amplitude $h_0 = 3$ Oe could be regarded as weak far from T_C and strong in the direct vicinity of this temperature. We recall (see Ref. 1) that in our experiments the Curie point was deduced from the temperature of the maximum of the signal of any higher harmonic (usually third or fifth) when the sample was subjected to a weak lf magnetic field.

It is clear from the results reported in Ref. 1 that in the scaling region (when we have $\tau > 1\times 10^{-2}$) it was possible to record reliably only the third and fifth harmonic, but the ratio r_5/r_3 [see Eq. (2a)] was fairly high, of the order of 10^2–10^{-3}, indicating a strong rise of the amplitudes of higher correlations as the correlation order increases.

We now turn to the results of the present study. The magnetization spectrum exhibited harmonics with fairly high values of n only in the anomalous region. A characteristic feature of the high harmonics in this spin-glass-like range of temperatures was a weak fall of the amplitudes of the harmonics with increasing harmonic number (Fig. 1 shows, by way of example, a fragment of the spectrum obtained for $\tau\approx 1\times 10^{-4}$ and $h_0 = 3$ Oe). Moreover, the absolute amplitudes of the harmonics were high. For example, for $\tau\approx 1\times 10^{-4}$ the ratio of the amplitude of the third harmonic

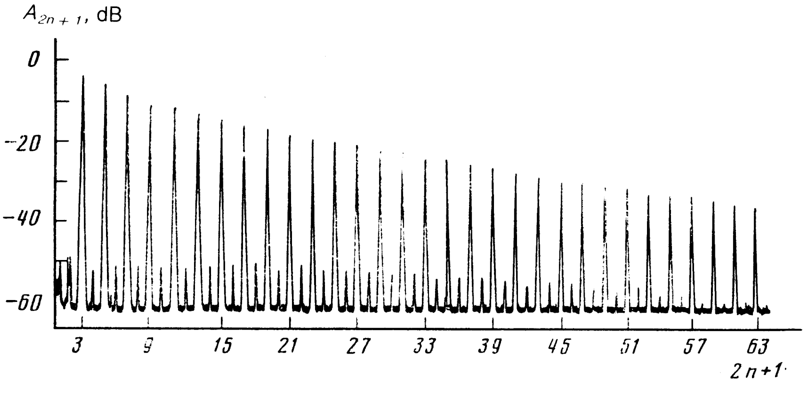

FIG. 1. Fragment of the spectrum of an emf induced in a measuring coil on application of an oscillatory magnetic field of amplitude $h_0 = 3$ Oe to a sample of $CdCr_2S_4$; f_0 1.6 kHz, $\tau\approx 1\times 10^{-4}$. The spectrum shows also the even harmonics induced by the residual (after screening) geomagnetic field.

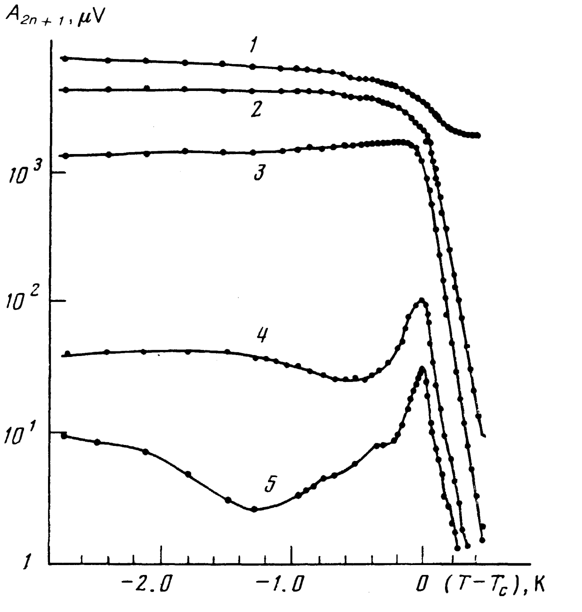

FIG. 2. Temperature dependences of the amplitudes of the following harmonics: 1) $(2n+1)=1$ (fundamental frequency 1.6 kHz); 2) $(2n+1)=3$ (4.8 kHz); 3) $(2n+1)=9$ (14.4 kHz); 4) $(2n+1)=53$ (84.8 kHz); 5) $(2n+1)=81$ (129.6 kHz); $h_0 = 3$ Oe.

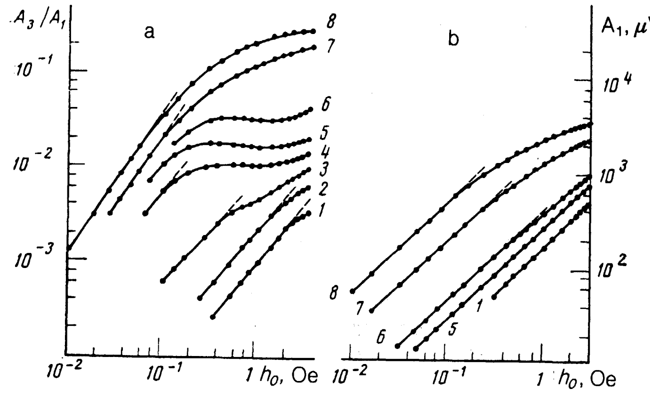

FIG. 3. a) Dependence of the ratio of the amplitude of the third harmonic to the fundamental frequency signal ($f_0 = 25.65$ kHz) on the amplitude of the oscillatory field obtained for different values of τ: 1) 6×10^{-3}, $(T-T_C)=0.50$ K; 2) 5.5×10^{-3}, $(T-T_C)=0.46$ K; 3) $5\times10^{-3}(T-T_C)=0.42$ K; 4) 4.5×10^{3}, $(T-T_C)=0.38$ K; 5) 4×10^{-3}, $(T-T_C)=0.34$ K; 6) 3×10^{-3}, $(T-T_C)=0.25$ K; 7) 2×10^{-3}, $(T-T_C)=0.17$ K; 8) $\approx1\times10^{-4}$, $(T-T_C)\approx0.1$ K. b) Dependence of A_1 on h_0 for different separations from T_C (the numbers of the curves correspond to the same values of τ as in Fig. 3a; the dependence of A_1 on h_0 is not plotted for curves 2, 3, and 4 because the values of A_1 are similar for the corresponding τ); $f_0 = 25.65$ kHz.

to the amplitude of the emf at the fundamental frequency was at least 0.1, whereas in the scaling region for $\tau\approx1\times10^{-2}$ this ratio was of the order of 10^{-3}.

It should be pointed out that the temperature dependence of the higher harmonics recorded in the presence of a sufficiently strong oscillatory magnetic field ($h_0 = 3$ Oe) depended strongly on the number of the harmonic. It is clear from Fig. 2 that in the direct vicinity of T_C the amplitudes of the higher harmonics $[(2n+1)f_0 \sim f_0]$ were practically independent of temperature. However, as the harmonic number increased, the dependence $A_{2n+1}(T)$ below T_C began to exhibit a maximum which shifted toward the Curie point, deduced under weak field conditions from the maximum of the third or fifth harmonic of the emf, on further increase in the harmonic number; finally, at high harmonics $[(2n+1)f_0 \gg f_0]$ the position of a clear maximum in the dependence $A_{2n+1}(T)$ did not vary with the harmonic number. Therefore, the high harmonics seemed to "forget" that the field at the fundamental frequency did not satisfy the weak-field criterion. However, we could not identify the reasons for such very different temperature dependences of the high and low harmonics observed in the presence of an oscillatory field of amplitude which in the direct vicinity of T_C was much higher than the scaling critical value defining weak fields.

The influence of the amplitude of an oscillatory magnetic field on the spectrum of higher harmonics is very important. With this in mind we investigated the changes in the amplitudes of the components of the spectrum at the fundamental frequency $f_0 = 1.6$ kHz when the field amplitude was increased from 0.3 to 3 Oe. Moreover, at 25.65 kHz a detailed study was made of the influence of the field intensity on the amplitude of the third harmonic, but in this case the range of h_0 was much wider (from 10^{-2} to 3 Oe). The results of these investigations, carried out at different frequencies, indicated that in the range 10^2–10^5 Hz the field dependences of the higher harmonics in the anomalous temperature region are independent of the field frequency and generally also independent of the harmonic number. Therefore, we shall consider the results of these investigations only in the case of the third harmonic.

Figure 3a shows the field dependence of the ratio of the amplitude of the third harmonic to the signal at the fundamental frequency A_1 whereas Fig. 3b gives the field dependence of A_1. Clearly, in the weak-field case, when we could represent the magnetization by a series in odd powers of h_0, the amplitude of the third harmonic should be proportional to the cube of the field and, consequently, we should have $A_3/A_1 \propto h_0^2$. However, it was shown in Ref. 2 that even in the normal temperature region when $\tau > 1\times10^{-2}[(T-T_C) > 0.8$ K$]$ the dependence of A_3 on h_0 was not purely cubic and the exponent in the power law describing this dependence was approximately 2.5. The same power exponent was found in the anomalous region above T_C, with the exception of the interval $0.2 \leqslant (T-T_C) \leqslant 0.4$ K, where the nonlinear response in weak fields was extremely small and, consequently, it was impossible to find an interval of the values of h_0 where the dependence $A_3(h_0)$ would be close to cubic. Generally speaking, the power-law dependence of A_3 on h_0 with an exponent of 2.5 was observed only in a certain range of the field amplitudes, and the range depended on temperature. At higher values of h_0 the dependence $A_3(h_0)$ became different (Fig. 3a). We were therefore justified in defining the critical field amplitude as that amplitude of the oscillatory field which corresponded to the onset of deviation from the near-cubic dependence of the amplitude of the third harmonic on the field amplitude.

The temperature dependence of the critical field h_{cr} defined in this way is plotted in Fig. 4. It is worth noting particularly the very strong reduction in h_{cr} at temperatures corresponding to the transition from the scaling range of critical phenomena to the anomalous region (spin-glass-like). In this case the critical field was considerably less than h_{cr} deduced from the scaling considerations. Nevertheless,

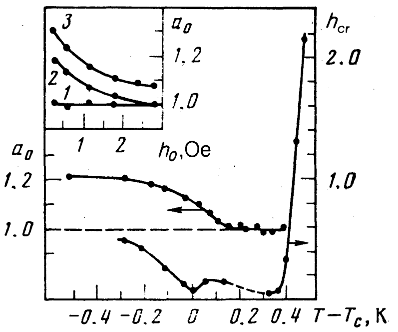

FIG. 4. Dependence of h_{cr} and a_0 on $T-T_C$. The inset gives the dependence of a_0 on h_0 for different values of $T-T_C$ (K): 1) 0.34, $\tau=4\times10^{-3}$; 2) 0.08, $\tau=1\times10^{-3}$; 2) ~0.01, $\tau\sim1\times10^{-4}$.

in the direct vicinity of T_C the value of h_{cr} deduced from the field dependence of the amplitude of the third harmonic was of the same order of magnitude as the value obtained from the scaling criterion. Clearly, this was why the temperature position of the maximum of the signal representing the third or fifth harmonic in a weak (in accordance with the scaling criterion) magnetic field was independent of the field amplitude.

The interval of the field amplitudes in which the fundamental-frequency signal increased linearly with h_0 was generally wider compared with the range of h_0 where a power-law dependence $A_3(h_0)$ had an exponent 2.5 (compare Figs. 3a and 3b). Moreover, A_1 varied linearly with h_0 even in a narrow temperature interval ($0.2 \leqslant T-T_C \leqslant 0.4$ K), where the ratio A_3/A_1 was practically independent of the field amplitude. In our opinion, this circumstance must be allowed for since, if we consider only the dependence $A_1(h_0)$, we can generally draw an incorrect conclusion of whether the field used in the investigations is weak or strong. It should be pointed out once more that the field dependence exhibited by harmonics with much higher numbers, determined in experiments using the fundamental frequency $f_0 = 1.6$ kHz and fields in the range $0.3 < h_0 \leqslant 3$ Oe, was of the same form as in the case of the third harmonic (when $f_0 = 25.65$ kHz).

As pointed out already, in the anomalous temperature region the amplitude of the higher harmonics decreased weakly with increasing the harmonic number (frequency). Therefore, it seemed of interest to provide somehow a quantitative description of the fall of the harmonic amplitudes in the spectrum. An analysis of the spectra with a large number of harmonics indicated that, within the limits of the experimental error ($\approx 10\%$), the ratio of the amplitudes of two consecutive harmonics can be represented by the following expression throughout the investigated range of temperatures:

$$\frac{A_{2m+1}}{A_{2m+3}} \equiv \frac{a_n}{a_{m+1}} = a_0 + b_0/m \qquad (3)$$

(here, m is the serial number of the odd harmonic, which has the value $m = 1, 2, 3, \ldots$). It follows from Eq. (3) that a_0 represents the limiting (corresponding to $m \to \infty$) value of the ratio of the amplitudes of two consecutive harmonics. It is clear from Fig. 4 that in a fairly narrow temperature interval near the transition to the anomalous region the value of a_0 is very close to 1 (we found that $a_0 = 1.00 \pm 0.02$). In this case (i.e., when $a_0 \sim 1$) we can use the methods for analyzing the convergence of positive numerical series (see, for example, Ref. 6) and show that a series composed of the moduli of the amplitudes of the higher harmonics is located near its convergence limit. Therefore, we can obviously say that the amplitudes of the harmonics decrease more slowly near the boundary between the scaling and anomalous temperature regions.

At lower temperatures, beginning from $T-T_C \approx 0.2$ K the ratio a_0 exceeds 1 and in the ferromagnetic phase it depends weakly on temperature, i.e., the amplitudes of the harmonics decrease more rapidly with increasing n than in that range of temperatures where a_0 is close to 1.

The limiting value of the ratio of the amplitudes of consecutive harmonics as a function of the field (inset in Fig. 4) shows that at temperatures close to T_C the value of a_0 decrease with increasing on increase in the field amplitude and approaches asymptotically a certain limiting value (curves 2 and 3 in the inset). On the other hand, in the temperature interval corresponding to the change in the nature of the critical values (curve 1 in the inset) the value of a_0 is very close to 1 and is independent of the field amplitude even when this amplitude is varied by a factor of 10.

In a quantitative estimate of the contribution of the nonlinear response it is usual to employ a nonlinear-distortion[7] coefficient

$$K_h = \left(\sum_n A_{2n+1}^2 / A_1^2 \right)^{1/2}, \qquad (4)$$

which represents the fraction of the field energy dissipated in the form of higher harmonics.

Using Eq. (4) to determine the coefficient K_h from the experimental spectrum, we can then study its temperature dependence. It is clear from the dependence of K_h on $(T-T_C)$ shown in Fig. 5 that this coefficient was highest near T_C. In this range we found $K_h > 1$, indicating a strong transfer of the field energy to the higher harmonics in the direct vicinity of T_C. The dependence of K_h on h_0 was of the same nature as the dependence $a_0(h_0)$. Clearly, as demonstrated by the inset in Fig. 5, showing the field dependence of the reduced nonlinear distortion coefficient $K_h^r = K_h(h_0)/K_h(h_0 = 3$ Oe), in the transition temperature interval $[0.2 \leqslant (T-T_C) \leqslant 0.4$ K$]$ the nonlinear distortion coefficient

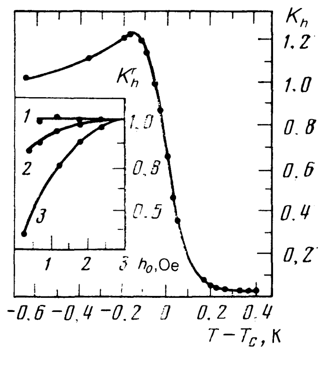

FIG. 5. Dependence of K_h on $T-T_C$; $f_0 = 1.6$ kHz. The inset shows the dependences of the reduced values K_h^r on the amplitude of the oscillatory field for different values of $T-T_C$ (K): 1) 0.34, $\tau=4\times10^{-3}$; 2) 0.08, $\tau=1\times10^{3}$; 3) ≈ 0.01, $\tau\approx1\times10^{-4}$.

was independent of the field amplitude when the field was increased from 0.3 to 3 Oe (curve 1). Away from this transition interval the coefficient K_h increased with h_0 (curves 2 and 3) or with a_0 approaching a certain limiting value at a given temperature.

The results of our investigation thus demonstrated that a ferromagnet near its phase transition is indeed a strongly nonlinear medium. However, the most interesting result is that the nonlinear properties of the susceptibility are manifested most strikingly at temperatures corresponding to the anomalous region. In fact, a very low value of the critical field occurs in this region and the amplitudes of the higher harmonics decrease most slowly as the harmonic frequency increases (at least in the range up to 10^5 Hz).

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