Some features of the behavior of the thermal conductivity of ferrites in the vicinity of magnetic phase transitions

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Results are presented of a study of the thermal conductivity of various ferrites with spinel structure. The measurements were made in the range from helium to high temperatures. Special attention is paid to the behavior of the thermal conductivity in the vicinity of various phase transitions. The effect of a magnetic field on the thermal conductivity was investigated to assess the role of spin thermal conductivity and to identify the mechanism of phonon scattering in the magnetic critical region. The experimental results are compared with the theory for large distances from the phase transitions as well as in the vicinity of the latter. The temperature dependence of the phonon mean free path is calculated. The anisotropy of the thermal conductivity of magnetite is investigated in the low-temperature transformation region. It is shown that the qualitative features of the thermal conductivity near the magnetic phase transitions points are closely related to critical scattering of thermal phonons by thermodynamic critical fluctuations of the spin-system energy density.

1. INTRODUCTION

Much progress was made in recent years in the study of equilibrium properties in the vicinity of magnetic phase transitions. Much was also accomplished in the study of certain particular problems that touch upon the dynamic behavior of a system in a magnetic critical region, for example the velocity and absorption of ultrasound. For the study of the dynamics of a spin system in the critical region it is natural to make use also of other kinetic parameters, including the thermal conductivity. It is then possible to obtain information that cannot be extracted by other means. This pertains, in particular, to the determination of the singularities of phonon scattering in the critical region.

In contrast to the critical liquid-vapor transition, where the situation is more or less clear[1], experimental data on the thermal conductivity of magnetic materials at the Curie (Neel) point are contradictory[2-10], apparently as a result of the known difficulties in the performance of precision experiments. It is also impossible to draw from the existing theoretical papers any conclusions concerning the existence of a universal law governing the behavior of the thermal conductivity in the region of the Curie point. Thus, for example, dynamic scale invariance predicts a divergence of the transport coefficients, including the thermal conductivity, at the Curie point[11], whereas other theoretical researches lead to different results[12-17].

This status of the problem demonstrates the need for new special experiments in the vicinity of magnetic phase transitions. In this article we present results obtained by us in recent years on the thermal conductivity of ferrites. Particular attention was paid to the influence of different phase transitions on the behavior of the thermal conductivity. We present also results of an investigation of the influence of the magnetic field on the thermal conductivity, which was carried out in order to isolate the role of the spin thermal conductivity, as well as to determine the mechanism whereby phonons are scattered in the critical region.

2. EXPERIMENTAL PROCEDURE

The measurements of the thermal conductivity (λ) in the region of low temperatures were carried out with a setup whose operating principle is based on an absolute stationary method. The setup ensured automatic stabilization of the temperature and the production of small temperature gradients on the investigated sample. Isothermy of the faces of the sample adjacent to the heater and the cooler was ensured by coating these faces with a metallic film to which the junctions of the copper-constantan thermocouples were soldered. The resultant heat losses were reduced to a minimum by semiconducting guard plates, which developed a large thermoelectric power, and by ensuring equality of the average temperature of the sample, to the ambient temperature. The temperature gradient at the sample was determined by the character of the temperature dependence of λ and did not exceed $0.2-1°K$. A detailed description of the instrument and of the low-temperature cryostat is given in[18]. The temperature in the helium range was measured with the aid of Allen-Bradley carbon resistance thermometers.

High-temperature measurements were performed with a similar installation, but with allowance for the specifics of these measurements[19]. It should be noted that although the specifics of the direct measurements of the thermal conductivity do not make it possible to come arbitrarily close to the critical point, nonetheless, in the vicinity of this point it is possible to study the essential details of the behavior of λ. The construction of the setup used for the measurement of λ in a magnetic field H differs from the earlier ones and is based on the quasi-pulsed method considered in[20].

3. SAMPLES

The investigations were performed on ferrites with spinel structure. Their ferromagnetic structure, naturally, should lead to certain singularities in the temperature dependence and field dependence of λ. The influence of the magnetic field becomes particularly clearly manifest at the Curie point T_C. However, too low and too high values of T_c are inconvenient from the point of view of the experiment. Solid solutions have the advantage that their values of T_c vary from composition to composition in a wide range. We therefore prepared for the investigation samples of stoichiometric composition with the general formulas $Ni_{1-x}Zn_xFe_2O_4$ and $Cu_{1-x}Cd_xFe_2O_4$, where x ranged from 0 to 1. The manufacturing technology was ceramic. We used for the investigation single crystals and polycrystals of natural magnetite.

It should be noted that prior to our investigations there were no measurements of λ of ferrites at the Curie point.

4. BEHAVIOR OF THERMAL CONDUCTIVITY FAR FROM MAGNETIC PHASE TRANSITIONS

Investigations of the thermal conductivity far from the magnetic phase transitions are necessary not only from the point of view of completeness of the research, but also in principle to estimate the normal course of λ, since it is difficult to estimate the anomalous region of λ without knowing this course, and also to separate the different contributions made to λ. In addition, it is necessary to verify the extent to which the discussed anomaly on the λ(T) curve is isolated. The proximity of other possible transitions greatly distorts the critical singularities and thus makes it difficult to assess this anomaly.

Typical measurement results, in a wide temperature interval, are shown in Figs. 1 and 2. We start the discussion with the data on Fe_3O_4, since they are the most typical.

Magnetite is a ferrimagnet and has an inverted-spinel structure. Each unit cell contains eight Fe^{3+} ions in tetrahedral (A) voids and eight Fe^{2+} and Fe^{3+} ions

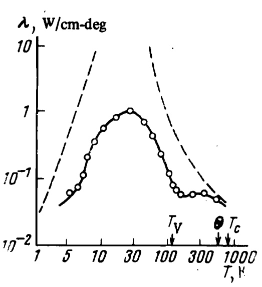

FIG. 1. Temperature dependence of the thermal conductivity of magnetite. Points—experiment, dashed curve—theoretical.

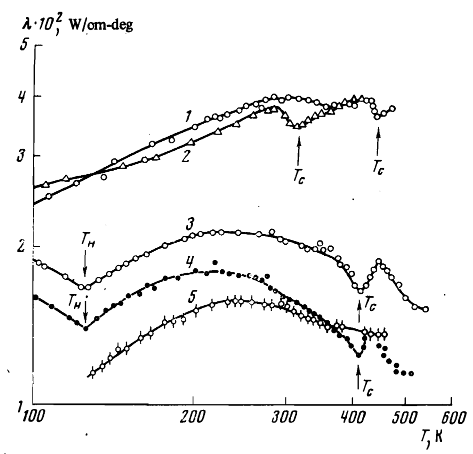

FIG. 2. Temperature dependence of the thermal conductivity of solid solutions: 1—$Ni_{0.4}Zn_{0.6}Fe_2O_4$, 2—$Ni_{0.3}Zn_{0.7}Fe_2O_4$, 3—$Cu_{0.6}Cd_{0.4}Fe_2O_4$, 4—$Cu_{0.5}Cd_{0.5}Fe_2O_4$, 5—$Cu_{0.2}Cd_{0.8}Fe_2O_4$.

each in octahedral (B) voids. The magnetic properties are explained on the basis of superexchange theory. Owing to the antiferromagnetic cation-anion-cation interaction, the magnetic moments of the ions in the A and B positions are antiparallel. The resultant magnetic moment is thus due to the Fe^{2+} ions in the B positions. In stoichiometric Fe_3O_4, the Fe^{2+} ions amount to 24.2%, whereas in our sample the concentration of the Fe^{2+} ions was 28%, and that of Fe^{3+} was 68.5%. The lattice constant equals 8.39 Å. The elastic-anisotropy factor is estimated by us at 0.84. It approaches unity with increasing temperature. The characteristic temperature T_D, determined from the elastic constants, is 526°K and depends weakly on the temperature. The thermal conductivity λ of magnetite was investigated in a number of studies[21,22]. In the present work we paid particular attention to the behavior of λ in the region of the low-temperature transition, to the anisotropy, and to the dependence of λ on H. The dependence of λ on T and H is important also because it should be common to other inverted-spinel ferrites.

The thermal conductivity of Fe_3O_4 was measured by us in the interval 5–500°K (Fig. 1). The absolute value of λ at room temperature was close to Slack's data[21]. Below the Verwey temperature (T_V), the value of λ for Fe_3O_4 reaches a maximum, and then decreases, this behavior being typical also of diamagnetic crystals. The amplitude of the low-temperature "hump" is determined by the defects and impurities of the crystal. What is unusual, however, is the λ(T) dependence in the interval $119°K \le T \le 300°K$, i.e., above T_V. In this interval λ(T) varies quite insignificantly. As is well known, the distribution of Fe^{2+} and Fe^{3+} over the octahedral and tetrahedral voids is random above T_V, and this probably enhances the anharmonicity of the Fe^{2+} and Fe^{3+} vibrations and limits strongly the phonon mean free path. In the presence of three-phonon interaction, the expression for the phonon mean free path l_{ph} was obtained by Leibfired and Schlömann[23], who found it to be inversely proportional to T. Calculation by their formula yields $l_{ph} \approx 0.6 \times 10^{-6}$ cm at $T \approx 300°K$. Calculation by the simple Debye formula gives a value which is smaller by one order of magnitude than the theoretical one and approaches the minimum possible according to Debye. The data on the specific heat C_{ph} were taken from[24], and those on the velocity v_{ph} from[25]. In the entire temperature interval, the theoretical value of l_{ph} is also higher than the experiment one. This indicates that in addition to the three-phonon interaction processes, an appreciable contribution is made also by other supplementary mechanisms that limit l_{ph} (scattering by vacancies, by magnetic inhomogeneities, by impurities, etc.). The low values of l_{ph} are probably also due to the complicated structure of the spinel-lattice unit cell itself. Above T_V, the temperature dependence of l_{ph} is also weak, which leads to a weak λ(T) dependence. In the interval 60–10°K, l_{ph} varies exponentially, just as in Slack's work[21].

At T > 350°K, λ begins to decrease noticeably. Above this temperature, the semiconductor resistivity ρ(T) of the investigated Fe_3O_4 gives way to metallic resistivity (Fig. 3). It is quite probable that the electron-phonon interaction is enhanced here, but the electronic thermal conductivity λ_e, of the Wiedemann-Franz type, is much lower than the experimental one even at these temperatures. The measurements results for $T < T_V$ can be satisfactorily explained by assuming that the principal role in the heat transfer is played by the phonons that are scattered in standard fashion, namely by scattering of the phonons by phonons (Umklapp processes), isotopes, vacancies, chemical impurities, and magnons. The dashed curve in Fig. 1 shows the upper limits of λ due to the Umklapp processes and scattering by the grain boundaries or by the boundaries of the sample itself. The scattering by the boundaries was calculated under the assumption of diffuse reflection of the phonons from the sample boundaries, $L \approx 0.24$ cm, and the contribution of the Umklapp processes was calculated using the value $\lambda_{TD} = 0.06$ W/cm-deg, which was taken from Slack's paper[21]. The experimental curve lies much lower than the theoretical one, obviously because of the nonstoichiometric composition of the sample and of its magnetic structure, which is not taken into account in the theory.

To assess the role played by the spin system in λ, we investigated the influence of the field H on the thermal conductivity of Fe_3O_4—the Maggi-Rigghi-Leduc (MRL) spin effect. The results of these measurements are shown in Fig. 4. The ordinates represent the MRL spin effect $\Lambda = (\Delta T_H - \Delta T_0)/\Delta T_0$, where ΔT_H is the difference of the temperatures on the sample in a magnetic field, and ΔT_0 is the difference without the field. The negative sign of Λ indicates that an appreciable role is played by spin-phonon interaction in the absence of the field. The increase of the absolute magnitude of Λ, up to 11°K, can be ascribed to the dragging of the magnons by the phonons and to the increase of the mean free path connected with the phonon-magnon interaction. Further increase of the temperature leads to inversion of the sign of Λ. At the temperature T_V we have $\Lambda = 0$—the additional contribution to λ induced by the field H vanishes. The positive sign of Λ can be attributed to suppression, by the field, of the role of the important magnon carriers in the heat transfer. We emphasize also the influence of the magnetoelastic modes on the thermal conductivity, which consists in an initial decrease of λ when the field H is applied[26,27]. Coupled modes limit the contribution of the carriers whose frequencies are close to the Larmor frequency in the paramagnetic phase, and of magnons and phonons with equal frequencies and wave vectors in the ordered phase. The last case characterizes the region of intersection of the magnon and phonon branches in the Brillouin zone. The quantity λ increases up to 180°K, after which it decreases; this is a reflection of the temperature dependence of the spin thermal conductivity λ_S and of the intensity of the interaction of the spin system with the lattice. At $T \geq 77$°K we have $\Lambda < 1\%$. Thus, the contribution of the pure spin waves to λ is negligibly small already at this temperature.

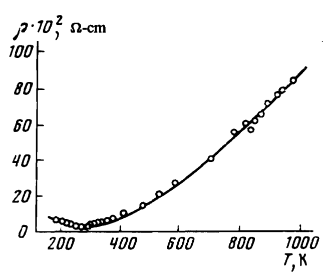

FIG. 3

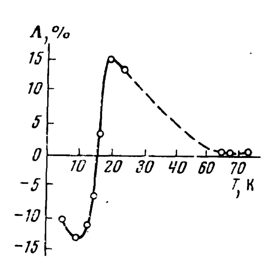

FIG. 4

FIG. 3. Temperature dependence of the resistivity of magnetite.
FIG. 4. Temperature dependence of the relative change of the thermal conductivity of magnetite in a magnetic field.

5. THERMAL CONDUCTIVITY OF Fe_3O_4 IN THE REGION OF THE LOW-TEMPERATURE TRANSITION

Magnetite was thoroughly investigated by a number of workers in connection with the low-temperature transition in the region 110—120°K (T_V). Initially this transition was described as an ionic transition of the order-disorder type, in which the low-temperature phase consisted of alternately ordered rows of Fe^{2+} ions in B-voids. In the high-temperature phase, they are randomly distributed in the B-sublattice. In subsequent studies, many refinements were introduced into this picture. In particular, one of the initial Vervey premises, namely the ordering of the ions in the B sublattices, is dispensed with in the band description of the transition[28], and account is taken of the doubling of the c axis in the phase transition, which leads to a breaking of the Brillouin zone and to the appearance of a gap. From this point of view, the phase transition is regarded as a metal-nonmetal transition, which results from Wigner electron crystallization[28], or as a transition of the Fröhlich type[29]. Experiment has shown the low-temperature phase transition in magnetite to be of first order and close to the critical point.

We describe below the results of low-temperature investigations conductivity of single-crystals along the three principal crystallographic directions [111], [110], and [100], as well as of a polycrystalline sample (Fig. 5). The $\lambda(T)$ curve for the polycrystal lies below the curves for the single crystal, this being probably due to the additional scattering of the phonons by the imperfections of the polycrystalline structure. A noticeable minimum of λ is observed in the region of the transition, but on going to the low-temperature phase there is observed a sharp increase of λ, especially in the [110] and [111] directions. In addition, the transition is stretched out on both sides of T_V.

This variation of λ can be explained on the basis of the scattering of the phonons by fluctuations of the order parameter and conservation of the short-range order, especially in the high-temperature phase. The longitudi-

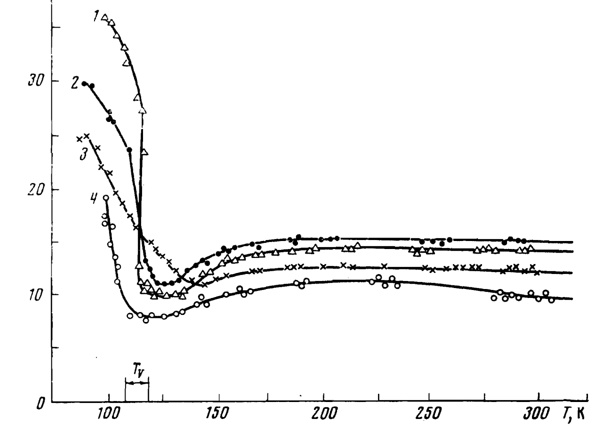

FIG. 5. Thermal conductivity of magnetite: 1) along [111], 2) along [110], 3) along [100]; 4) polycrystal.

nal oscillation mode can increase the overlap integral and cause a partial ordering of the octahedral ions. This type of phonon scattering can take place not only in the transition region itself, but also at $T > T_V$. From the results of the measurements of λ it is seen that this scattering probably varies very little up to the Debye temperature, but at $T > T_D$ it should be masked by Umklapp processes, a fact noted already by Slack[21].

The anisotropy of λ and its absolute values along the principal crystallographic directions in the transition region are apparently determined by similar mechanisms as the sound propagation velocities. This follows from the results of measurements of the sound velocities in the same samples (Fig. 6). The sound velocity was measured with the setup described in[31].

Along the [111] and [110] directions, the minimum of λ, just as the minimum of the longitudinal-sound velocity, appears at T = 114°K. For the [100] direction, a slight minimum of λ occurs at 148°K. It is possible that it is precisely in this direction that the longitudinal phonons lead relatively easily to a growth of the overlap integral, which should contribute to the conservation of the long-range order. This also is confirmed in part by the fact that the minimum of the longitudinal-sound velocity in this direction occurs at a higher temperature. This fact also offers evidence that the artificial production of longitudinal oscillations leads to a delay of the phase transition. That the transverse waves do not make a special contribution to this process can be seen from the fact that a minimum is observed in their propagation velocity in the [100] direction at a lower temperature, namely 136°K. Finally, the change of λ, just as that of the longitudinal velocity, at the transition temperature is considerable for the diagonal planes.

We can thus conclude that the investigation of λ reveals certain essential details of the low-temperature phase transition in Fe_3O_4.

6. THERMAL CONDUCTIVITY OF FERRITES IN TRANSITIONS FROM A NONCOLLINEAR MAGNETIC STRUCTURE TO A COLLINEAR ONE

The low-temperature transition in magnetite proceeds with conservation of the collinearity of the magnetic moments of the sublattices. Such transitions are not numerous in ferrites, which are much more frequently subject to transitions that affect the magnetic structure. Thus, for example, in mixed ferrites one can encounter transitions from the collinear magnetic structure to the noncollinear one[32]. The impetus for the consideration of such structures was provided by the ideas of "weak ferromagnetism"[33]. We present here plots of the behavior of λ near such transitions.

Interesting objects for these investigations turned out to be mixed ferrites of the copper-cadmium system, $Cu_{1-x}Cd_xFe_2O_4$. The ferrites of this system are inverted spinels, with the exception of $CdFe_2O_4$, with relatively large lattice parameters and low values of the exchange energy between the sublattices, which creates conditions for the appearance of noncollinearity of the magnetic structure. Indeed, the behavior of the magnetic and magnetoelastic properties confirms the existence in these ferrites of a phase transition of the "star" type, analyzed in[35], from the collinear to the noncollinear structure in the vicinity of 120°K[34]. The general course of $\lambda(T)$ of these samples is illustrated in Fig. 2.

The low-temperature minima on the $\lambda(T)$ curves are connected with the ferrimagnet-paramagnet transition (T_C). It should be noted that unlike $\lambda(T)$ of magnetite, we observe here in the main a monotonic decrease of λ from room temperatures to 78°K. A similar course of $\lambda(T)$ was found also for other mixed ferrites[7,21]. It is known that these ferrites are inverted or partially inverted. It is possible to encounter in them inhomogeneities in the distribution of the ions in the octahedral and tetrahedral positions, as well as local fluctuations in the magnetic sublattices, which serve as effective centers of phonon scattering and strongly limit l_{ph}. In this case λ decreases mainly monotonically with decreasing T.

The behavior of λ in the region of the phase transition from the collinear to the noncollinear structure, which is magnetic transition of the order-disorder type, in ferrites of the $Cu_{1-x}Cd_xFe_2O_4$ system, reveals a noticeable minimum in the region of low temperatures T_L (curves 3 and 4 of Fig. 2). A fragmentary picture of the variation of $\lambda(T)$ in a narrower interval of temperatures T_L is shown in Fig. 7 for all the compositions. Against the background of the general course of $\lambda(T)$, these minima have approximately the same form as the minima on curves 3 and 4 of Fig. 2 near T_L. There are no minima of $\lambda(T)$ for $CdFeO_4$ and $Cu_{0.2}Cd_{0.8}Fe_2O_4$,

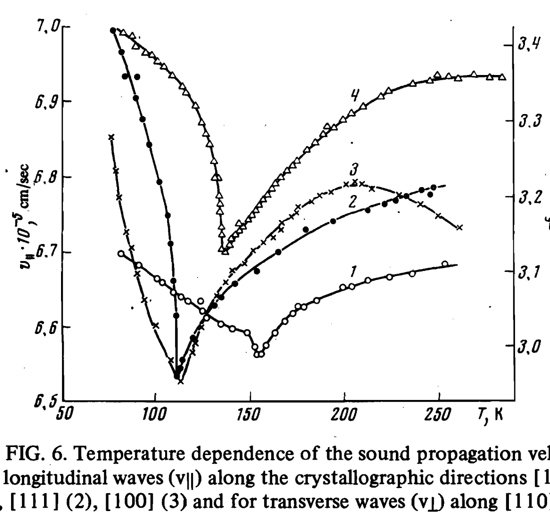

FIG. 6. Temperature dependence of the sound propagation velocities for longitudinal waves ($v_\parallel$) along the crystallographic directions [110] (1), [111] (2), [100] (3) and for transverse waves ($v_\perp$) along [110] (4). The ultrasound frequency is 5 MHz.

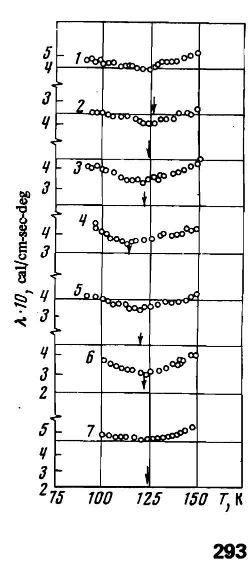

FIG. 7. Thermal conductivity in the region of the low-temperature transitions of $Cu_{1-x}Cd_xFe_2O_4$: 1–x = 0.1, 2–x = 0.2, 3–x = 0.3, 4–x = 0.8, 5–x = 0.5, 6–x = 0.6, 7–x = 0.7. The arrows show the temperatures at which the minimum of the thermal conductivity occurs.

for which the region 120°K and higher is paramagnetic. The foregoing results can be explained under the assumption that in these transitions there is observed an intensive development of processes that lead to phonon scattering and are connected with fluctuations of the characteristic order parameter, in this case the angle between the magnetic moments of the sublattices.

7. THERMAL CONDUCTIVITY IN THE REGION OF THE CURIE POINT

We have investigated the thermal conductivity of a number of ferrites in the vicinity of the Curie point. The results of these investigations are shown in Fig. 8. The temperature dependence of $\lambda(T)$ of all the ferrites has an anomalous form at the Curie point T_C. The Curie points of the samples, which were determined by us from magnetic measurements, also coincide with the positions of the minima on the $\lambda(T)$ curves. The anomalous course of $\lambda(T)$ at T_C is usually explained either on the basis of phonon scattering by the critical fluctuations of the energy density of the spin system[13,14], or as a result of magnon-phonon interaction[35,36]. In magnetic insulators, such as ferrites, there exists, owing to $\lambda_e = 0$, two mechanisms responsible for the spin-phonon coupling, namely one-ion and two-ion bonds.

The dominant mechanism of the spin-phonon coupling is established on the basis of a comparison of the constants B_V and $B_\perp$, which characterize respectively the volume-magnetostriction and linear-magnetostriction energy. To reveal the dominant mechanism of the spin-phonon coupling in the investigated ferrites, let us analyze the character of the spin-phonon interaction in these substances.

The volume-magnetostriction coupling constant B_V is determined from the dependence of the exchange interaction on the pressure or from the change of the volume, and is expressed in terms of the slope of the exchange integral J_{AB} in the following manner[37]:

$$B_V = Na\partial J_{AB}/\partial a, \tag{1}$$

where N is the number of particles per unit volume, a is the lattice constant, and $\partial J_{AB}/\partial a$ is estimated from the shift of T_C under the influence of the hydrostatic pressures[38,39]. An expression can also be obtained for B_V in the form

$$B_V = \frac{3N_A\rho}{M} J_{AB}\gamma, \tag{2}$$

where N_A is Avogadro's number, ρ is the density,

$$\gamma = \frac{\partial \ln J_{AB}}{\partial \ln V} = -\frac{1}{\varkappa}\frac{\partial \ln T_c}{\partial P} = \frac{10}{3},$$

and κ is the compressibility. According to our measurements $\kappa = 3/(C_{11} + 2C_{12}) = 7.6 \cdot 10^{-4}$ kbar^{-1} for Fe_3O_4[25].

The linear-magnetostriction constant is equal to

$$B_\perp = 2.4C_{44}\lambda_{m0}, \tag{3}$$

where λ_{m0} is the magnetostriction constant at 0°K.

We have calculated B_V and $B_\perp$ from these formulas for classical spinel and garnet ferrites. The results are listed in the table. Approximately similar relations between B_V and $B_\perp$ are obtained also for other ferrites, for which the elastic constants are given in[40]. By analyzing the coupling constants given in the table, we can conclude that the main mechanism of the spin-phonon coupling in the investigated ferrites is the volume-magnetostriction coupling, which results from phonon modulation of the exchange interaction between the magnetoactive ions. As is well known, this coupling mechanism contributes to the critical absorption of the phonons near T_C, and also to the emission and absorption of phonons by the scattering of spin waves. The theory of thermal conductivity near T_C with allowance for these processes was considered by Kawasaki[13], by Stern[14], and by Huber[17], who expressed the phonon scattering cross sections in terms of Fourier transforms of a four-spin or energy correlation function that depends strongly on $T - T_C$. In this case the connection with the order parameter or with the fluctuations of the spin-energy density leads to a critical scattering of the phonons near T_C. The character of $\lambda(T)$ obtained by us near T_C corresponds in general with these predictions, and we can therefore compare our results with the conclusions of the theory.

We shall assume that $\lambda = \lambda_s + \lambda_{ph}$. The relation between λ_s and λ_{ph} determines the form of $\lambda(T)$ at the point T_C. Kawasaki[13] calculated the contribution of the spin thermal conductivity λ_s to T_C within the framework of the theory of the molecular field for $T_C \ll T_D$ and obtained it in the form

$$\lambda_s = 9\tau k_B^2 T_c^2 / 4a\hbar^2 zS(S+1), \tag{4}$$

where τ is the microscopic relaxation time, k_B is Boltzmann's constant, a is the lattice constant, z is the number of nearest neighbors, and S is the spin number. By way of example we calculate λ_s in a ferrite with composition $Cu_{0.4}Cd_{0.6}Fe_2O_4$ near T_C, for which we have obtained the following parameters: T_C = 303 K, a = 8.60 Å, T_D = 600 K, z = 8, ρ = 5.11 g/cm³ and s = 5/2.

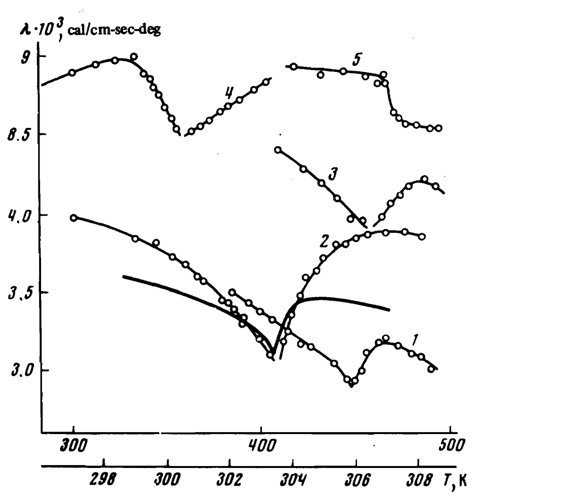

FIG. 8. Anomalies of the thermal conductivity in the vicinity of the Curie point: 1—$Cu_{0.5}Cd_{0.5}Fe_2O_4$, 2—$Cu_{0.4}Cd_{0.6}Fe_2O_4$, 3—$Cu_{0.6}Cd_{0.4}Fe_2O_4$, 4—$Ni_{0.3}Zn_{0.7}Fe_2O_4$, 5—$Ni_{0.4}Zn_{0.6}Fe_2O_4$. The thick curve was calculated in accord with [14]. The lower temperature scale pertains to curve 2.

Characteristic	Substance	
	Fe_3O_4	$Y_3Fe_5O_{12}$
$\partial \ln T_c/\partial P$, 10^{-3}/kbar	2.42	2.23
$-J_{AB}$, K	15	36
$\partial \ln J_{AB}/\partial \ln V$	10/3	10/3.2
B_V, 10^6 erg/cm³	281.5	151.2
$B_\perp$, 10^6 erg/cm³	20	1.28

The spin-lattice relaxation time $\tau = 4 \times 10^{-8}$ sec was obtained on the basis of measurements of the velocity and absorption of ultrasound in the vicinity of T_c[41]. The value of λ_s calculated from (4) is $\approx 10^{-5}$ cal/deg-cm-sec, as against the experimental value $\lambda \approx 4 \times 10^{-3}$. It follows therefore that the spin thermal conductivity at T_c can be neglected. This means that the rate at which the spin energy diffuses through the system is very low, although the corresponding specific heat is large. Therefore λ_{ph} behaves anomalously at the point T_c as a result of scattering of the phonons by critical fluctuations of the energy density of the spin system.

Using the measured values of λ, of the magnetic specific heat, and of the sound velocity v_{ph}[41], we have calculated the temperature dependence of the phonon mean free path $\bar{l}_{ph}$ near T_c using the formula $\bar{l}_{ph} = 3\lambda v_{ph}^{-1} C_{ph}^{-1}$. In this case C_{ph} is the phonon specific heat obtained from the total specific heat after subtracting the magnetic contribution C_m. The results are shown in Fig. 9.

Additional information concerning the role of the critical fluctuations in the thermal resistance $1/\lambda$ near T_c can be obtained from measurements of λ in the magnetic field H. Indeed, in the vicinity of T_c the MRL spin effect has a negative sign, thus confirming the dominant role of critical fluctuations in phonon scattering in a zero field, in the absence of the influence of coupled modes on near T_c. With increasing field H, the depth of the minimum decreases, indicating a lesser role of the critical fluctuations in the thermal resistance.

Finally, let us consider the connection between λ and the magnetic specific heat C_m, which follows from the Stern theory[14]. He obtained the following expression for λ near T_c:

$$\lambda = BT^{-3/2}(C_m T^2)^{-1/2}, \quad (5)$$

where B is a proportionality coefficient. For many of the investigated samples we have measured C_m. Since C_m has a maximum at T_c, it follows therefore also that λ should have a minimum at the Curie point. Using the obtained values of C_m, we have calculated λ by formula (5). The constant B in (5) was determined by substituting the experimental values of λ and C_m at temperatures where the new scattering mechanism becomes dominant. The calculated data are shown in Fig. 8 by the solid curve. It is seen that qualitative agreement exists with experiment. We note also that a maximum of the sound absorption and a minimum of the velocity are observed near T_c[41].

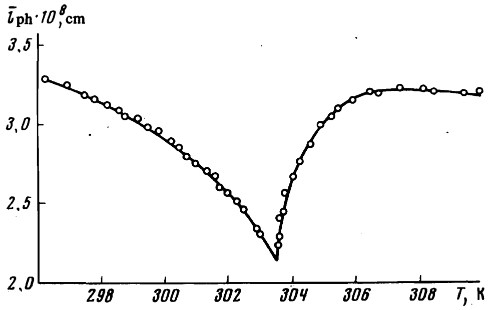

FIG. 9. Temperature dependence of the mean free path of the phonons in $Cu_{0.4}Cd_{0.6}Fe_2O_4$.

Summarizing the discussion of the experimental results, we can state that the qualitative features of the thermal conductivity near the points of magnetic phase transitions are closely connected with the critical scattering of the thermal phonons by thermodynamic critical fluctuations of the energy density of the spin system or of the order parameter, which appears as a scattering mechanism that supplements the already known mechanisms such as three-phonon, boundary, impurity, etc.

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[1] J. V. Sengers and P. H. Keyes, Phys. Rev. Lett., 26, 70 (1971).
[2] V. E. Mikryukov and N. M. Speranskiĭ, Inzhenerno-fiz. Zh. 6, 38 (1962).
[3] E. D. Devyatkova and V. V. Tikhonov, Fiz. Tverd. Tela 9, 772 (1967) [Sov. Phys.-Solid State 9, 604 (1964)].
[4] I. I. Vishnevskiĭ and V. N. Sripak, Fiz. Tverd. Tela 9, 3633 (1967) [Sov. Phys.-Solid State 9, 2865 (1968)].
[5] V. A. Shchelkotunov and V. N. Danilov, Izv. AN SSSR, seriya neorg. 7, 284 (1971).
[6] Ya. M. Bekker, Fiz. Tverd. Tela 7, 1545 (1965) [Sov. Phys.-Solid State 7, 1245 (1965)].
[7] I. K. Kamilov, Fiz. Tverd. Tela 4, 2312 (1962) [Sov. Phys.-Solid State 4, 1693 (1963)].
[8] F. B. Lewis and N. H. Saunders, J. Phys. C. (Sol. St. Phys.), 6, 2525 (1973).
[9] R. G. Moris and J. L. Cason, Jr., Helv. Phys. Acta. 411, 1045 (1968).
[10] K. Hirakawa, H. Mike, and H. Hayashi, J. Phys. Soc. Japan, 33, 266 (1972).
[11] P. Graig and W. J. Golaburg, J. Appl. Phys., 40, 964 (1969).
[12] M. A. Krivoglaz, Fiz. Tverd. Tela 2, 1200 (1960) [Sov. Phys.-Solid State 2, 1087 (1960)].
[13] K. Kawasaki, Progr. Theor. Phys., 29, 801 (1963).
[14] H. Stern, J. Phys. Chem. Sol., 26, 153 (1965).
[15] M. Inoue, Phys. Lett., 27A, 242 (1968).
[16] M. Takemura and K. Tani, J. Phys. Soc. Japan, 31, 151 (1971).
[17] D. L. Huber, Solid St. Comm., 6, 685 (1968).
[18] I. K. Kamilov, Prib. Tekh. Eksp. No. 3, 176 (1962).
[19] I. K. Kamilov, Peredov. Nauchno-tekhn. opyt (Progressive Scientific-Technical Experience), No. 32-63-294/4, Gosinti, 1963.
[20] E. E. Vishnevskiĭ, in: Teplo- i massoobmen v protsessakh ispareniya (Heat and Mass Exchange in Evaporation Processes), AN BSSR, 1958.
[21] G. A. Slack, Phys. Rev., 126, 427 (1962).
[22] V. L. Sedov, L. V. Solomatina, and L. I. Il'chenko, Zh. Eksp. Teor. Fiz. 43, 1125 (1962) [Sov. Phys.-JETP 16, 794 (1963)].
[23] G. Leibfried and E. Schlomann, Nachr. Acad. Wiss. Göttingen, Math.-Physik, Kl, 71 (1954).
[24] I. K. Kamilov, G. M. Shakhshaev, and Kh. K. Aliev, Teplofizicheskie svoĭstva veshchestva (Thermophysical Properties of Matter), Kiev, 1971, p. 192.
[25] I. K. Kamilov and Kh. K. Aliev, Fiz. Tverd. Tela 12, 1857 (1970) [Sov. Phys.-Solid State 12, 1478 (1970)].
[26] A. I. Akhiezer, V. G. Bar'yakhtar, and G. V. Peletminskiĭ, Spinovye volny (Spin Waves), Nauka (1967).

[27] G. S. Dixon, D. Walton, and J. E. Rives, J. Appl. Phys., 40, 1555 (1969).
[28] J. B. Sokoloff, Phys. Rev., B3, 3162 (1971); B5, 4496 (1972).
[29] D. Adler, Essays in Physics, 1, Academ. Press, New York, 1970, p. 33.
[30] W. P. Mason, Physical Acoustics and the Properties in Solids. D. Van Nostrand Company, Inc. Princeton, New Jersey, 1958.
[31] Kh. K. Aliev, E. A. Vasyuta, and I. K. Kamilov, Prib. Tekh. Eksp. No. 1, 249 (1973).
[32] K. P. Belov, Ferrity v sil'nykh magnitnykh polyakh (Ferrites in Strong Magnetic Fields), Nauka, 1972; J. Jafet and C. Kittel, Phys. Rev. 87, 290 (1952).
[33] A. S. Borovik-Romanov, Antiferromagnetizm i ferrity (Antiferromagnetism and Ferrites), in: Itogy nauki (Science Summaries), AN SSSR, 1962. I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. 33, 807 (1957) [Sov. Phys.-JETP 6, 621 (1958)].
[34] I. K. Kamilov, Kh. K. Aliev, G. M. Shakhshaev, M. M. Magomedov, and G. G. Musaev, Tezisy mezhdynarodnoĭ konferentsii po magnetizmu (Abstracts of Internat. Conf. on Magnetism), Moscow, 1973, p. 388.
[35] B. J. Boucher, R. Ruhle, and M. Perin, J. Chem. Sol., 30, 2467 (1969).
[36] G. Laurence and D. Petigrad, Phys. Rev., B8, 2130 (1973).
[37] B. Lüthi and R. J. Pollina, Phys. Rev., 167, 488 (1968).
[38] D. Bloch, J. Phys. Chem. Solids, 27, 881 (1966).
[39] G. A. Samara and A. A. Giardini, Phys. Rev., 186, 577 (1969).
[40] G. A. Petrakovskiĭ, Izv. AN SSSR, seriya fiz. 34, 1052 (1970).
[41] I. K. Kamilov, Kh. K. Aliev, and G. M. Shakhshaev, Fiz. Tverd. Tela 15, 914 (1973) [Sov. Phys.-Solid State 15, 632 (1973)].

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