Exotic specific heat anomaly in the GdY system: A probable signature of the Lifshitz transition

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The order-order magnetic phase transition "helical antiferromagnet–ferromagnet" in the Gd_xY_{1-x} system have been examined by means of the specific heat vs temperature. The observed anomaly in the specific heat does not follow the ordinary second-order transition scenario but resembles the exotic second-and-a-half–order behavior, according to the Ehrenfest's classification of the phase transitions. Such a behavior was first predicted for the Lifshitz electronic topological transition. We suggest that the observed anomaly is likely a product of the underlying Lifshitz transition associated with the magnetic phase transition.

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I. INTRODUCTION

The Lifshitz transition [1], also known as the electronic topological transition—the qualitative change of the Fermi surface (FS) shape under pressure, content, or temperature variation—is one of the basic phenomena of the physics of metals. In terms of the density of states, it occurs when Fermi level crosses the van Hove singularity, therefore providing characteristic anomalies in the physical properties of the metal.

In early studies the Lifshitz transition was considered as a rather exotic phenomenon that occurs only when Fermi level and the van Hove singularity appeared accidentally—or by precise choice of the object—to be very close to each other. Later it appeared to be more frequent; Lifshitz transitions have been observed experimentally in Bi and its alloys, in Al, Zn, Cd, As, In, in Re and its solid solutions, in LiMg and CdMg systems, etc., mostly under pressure and/or content variation [2–13]. The observations of the Lifshitz transition in Ti [14,15] and WTe_2 [16] were remarkable as manifestations of the "real" thermodynamic phase transition that occurs in temperature, not in pressure.

The general thermodynamic feature of the Lifshitz transition in temperature is a characteristic additional term proportional to $(T - T_1)^{5/2}$ in the free energy; T_1 hereafter corresponds to this phase transition [1]. According to the classical Ehrenfest classification [17] this transition deserves the name "second-and-a-half–order" transition. Consequently this transition is associated with the characteristic asymmetric square-root anomaly on the specific heat temperature dependence $c_p(T)$: $\Delta c_p(T) \propto (T - T_1)^{1/2}$ [1]. The case of the finite temperature is studied in [18].

In Fig. 1 we compare qualitative sketches of the $c_p(T)$ dependencies in the cases of (a) the ordinary second-order transition (considering our object, the lower-symmetry phase is situated at the higher temperatures, which is uncommon but feasible) and (b) the second-and-a-half–order transition, following [1]. In the most general description the second-order transition is reflected by a more or less broadened peak while the second-and-a-half–order transition is reflected by a sort of kink. In other words, in the case of the second-and-a-half–order transition the transition temperature is associated not with the local peak, but with the onset of the wide anomaly on the $c_p(T)$ dependence, which is a specific signature of this transition.

Being just an addition to the electronic specific heat of the given metal, which is in turn a tiny fraction of the total specific heat typically dominated by phonon contribution, this anomaly was expected unlikely to be observable experimentally. It is noteworthy that while the term "second-and-a-half–order transition" is often used as a synonym to the "Lifshitz transition," the second-and-a-half–order transition in the strict Ehrenfest's sense [i.e., a square-root anomaly on the $c_p(T)$ dependence] has not been observed, to the best of our knowledge.

In [19] we have suggested that the "helical antiferromagnet–ferromagnet" magnetic phase transition in the GdY system, believed to arise from the underlying Lifshitz transition, demonstrates the characteristic second-and-a-half–order transition behavior. In this work we are going to confirm this suggestion.

Heavy rare-earth *hcp* metals and their alloys with each other and relative yttrium are examples of solids in which the geometry of the Fermi surface directly determines the type of magnetic structure via "magnetic nesting" first proposed for chromium by Lomer [20] and for rare-earth metals by Dzyaloshinski [21] (see review [22]). It is well established that the various forms of complex periodic magnetic structures evident in these metals (i.e., helical, sinusoidal, cycloid etc.) all correspond to one plausible geometry of the FS, while the simple collinear ferromagnetic order is associated with the alternative shape of the FS (see Refs. [23–28] for details).

The phase transitions from the complex periodic magnetic structure to the simple collinear ferromagnetic phase with temperature are typical of the heavy rare-earth metals. In the straightforward approach it means that all of these transitions should be associated with the second-and-a-half–order transition, i.e., the Lifshitz transition from one plausible geometry of the FS to the alternative one. Actually the magnetic structures in these objects are typically subject to the strong magnetic anisotropy and therefore these transitions are

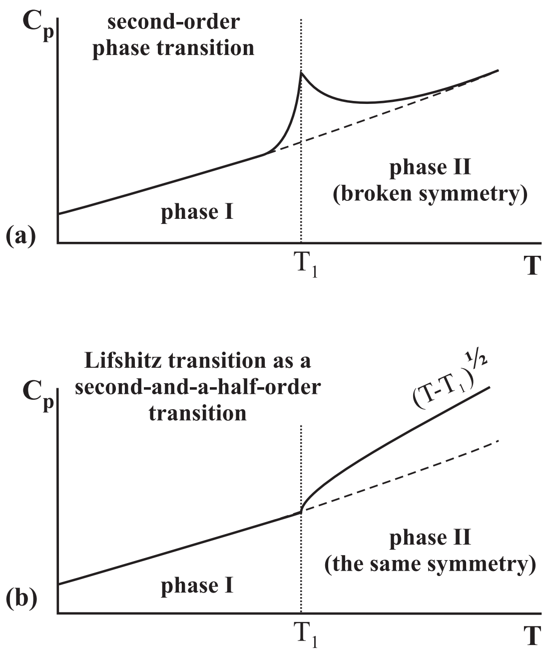

FIG. 1. Qualitative sketch of the temperature behavior of the specific heat in the vicinity of the phase transition: (a) phase transition at T_1 is second order (considering our object, the lower-symmetry phase is situated at the higher temperatures, which is uncommon but feasible); (b) phase transition at T_1 is a second-and-a-half–order transition, arising from the Lifshitz transition. Dashed line depicts a background dependence. T_1: temperature of the phase transition.

accompanied by drastic crystalline lattice distortions. As a result, these transitions in Tb, Dy, and their relatives are actually first order. However, Gd and its solutions with nonmagnetic yttrium are an important exception because the magnetic anisotropy in Gd is several orders of magnitude smaller than in the other heavy rare-earth metals due to its zero orbital moment [22].

The magnetic structures and phase transitions in the $Gd_{1-x}Y_x$ system were studied thoroughly in [29–34]. Compositions with $0.40 > x > 0.32$ do order magnetically into a helical antiferromagnetic state at T_N and then turn into a collinear ferromagnetic state at T_1 and remain ferromagnetic down to the lowest temperatures, which is typical for the heavy rare-earth metals. Nevertheless, it was clearly demonstrated in [32] that the "helical antiferromagnet–ferromagnet" transition in the $Gd_{66}Y_{34}$ system is definitely not first order in contrast with the other heavy rare-earth metals' solutions. In particular, no thermal hysteresis was observed on the smooth temperature dependence of the magnetic helical wave vector that approaches zero at T_1 [32]. The direct study of the FS in this system by positron annihilation [34,35] and angle-resolved photoemission spectroscopy [36,37] along with *ab initio* calculations [26] confirmed the change in the FS shape. Therefore, we suggested that the discussed magnetic phase transition, with the Lifshitz transition in the background, may be actually second-and-a-half–order [19]. The expected asymmetric square-root anomaly, according to the FS geometry, should be associated with the helical phase, i.e., located at $T > T_1$. The specific heat measurements were performed to check this suggestion.

II. EXPERIMENTAL DETAILS

The textured samples chosen for this study were cut from specimens of $Gd_{0.66}Y_{0.34}$, $Gd_{0.65}Y_{0.35}$, and $Gd_{0.69}Y_{0.31}$, prepared in Moscow Institute for Metals by O. D. Chistyakov from the components of 99.99% purity by arc melting and following annealing under the same conditions for all three specimens. (The specimens of $Gd_{0.66}Y_{0.34}$ and $Gd_{0.65}Y_{0.35}$ were the same as used in [19]; see detailed description and characterization therein.)

The magnetic states of the samples were examined by means of ac magnetic susceptibility temperature dependencies $\chi(T)$. The values of transition temperatures obtained from these dependencies are 201 ± 0.5, 202 ± 0.5, and 213 ± 0.5 K for the magnetic ordering temperatures; 125 ± 2, 152 ± 2, and 190 ± 2 K for T_1 for $Gd_{0.65}Y_{0.35}$, $Gd_{0.66}Y_{0.34}$, and $Gd_{0.69}Y_{0.31}$, respectively. These values match the "temperature-content" phase diagram obtained in [31] within $\pm 0.3\%$ content accuracy that proves the quality of the samples. Therefore, the magnetic ordering temperatures for all three samples vary within $\pm 3\%$; their Debye temperatures, according to density, within $\pm 1\%$; and their saturation magnetization values, according to content, within $\pm 3\%$, rather close to each other, while T_1 values vary drastically. It means that $Gd_{0.69}Y_{0.31}$, ferromagnetic from the lowest temperatures to 190 K, may serve as a reference object for the remaining two samples in this temperature range that includes the studied phase transition at T_1 in both of them.

The temperature dependencies of the specific heat were obtained with a PPMS Quantum Design relaxation calorimeter in a temperature range 2–270 K on heating, with and without magnetic field, using the same setup for all three samples. The temperature rise in a single measurement never exceeded 4 K.

III. RESULTS

The resulting $c_p(T)$ dependence for $Gd_{0.65}Y_{0.35}$ at $H = 0$ is presented in Fig. 2(a); the dependencies for the remaining two samples almost coincide with it on this scale. The peak at T_N is clear while the anomaly at T_1 is weak. Obviously there is no evidence of the first-order transition at T_1. Electronic specific heat coefficients γ at $T \to 0$ are 14 ± 2, 17 ± 3, and 12 ± 2 mJ/K^2 mol for $Gd_{0.65}Y_{0.35}$, $Gd_{0.66}Y_{0.34}$, and $Gd_{0.69}Y_{0.31}$ respectively; approximately the same value.

The detailed $c_p(T)$ dependencies for $H = 0$ and $H = 5$ kOe for all the samples in the vicinity of T_1 are presented in Fig. 2(b). The accuracy of these dependencies, estimated by data points spread, is about ± 0.2 [J/mol K], and calorimeter reported errors are about ± 0.1 [J/mol K]. We assume that $H = 5$ kOe magnetic field suppresses completely the helical antiferromagnetic phase in both the helically ordered samples in favor of the ferromagnetic phase. The anomaly in $c_p(T)$ associated with the magnetic transition at T_1 is well resolved at least for $Gd_{0.65}Y_{0.35}$, while for $Gd_{0.66}Y_{0.34}$ it is at the edge of the experimental accuracy. It is already clear that these anomalies do not resemble a peak at T_1 [Fig. 1(a)] and are closeer to the second-and-a-half–order behavior [Fig. 1(b)].

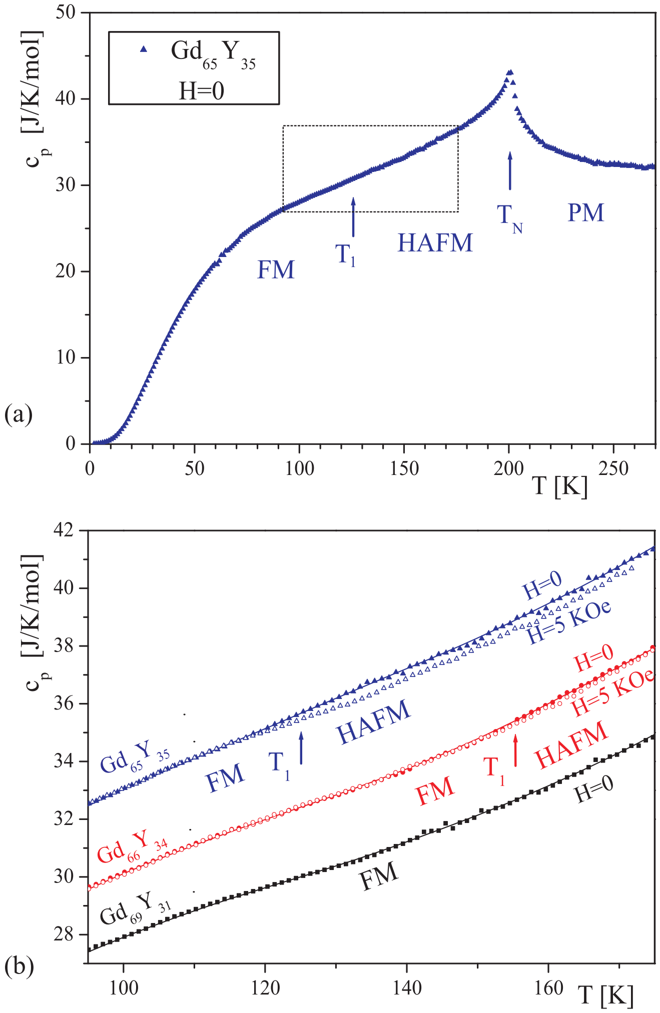

FIG. 2. (a) Temperature dependence of the specific heat $c_p(T)$ in zero magnetic field for $Gd_{0.65}Y_{0.35}$. $T_1 = 125 \pm 3$ K is the temperature of the helical antiferromagnet–ferromagnet transition, obtained independently by neutron scattering [29] and magnetic susceptibility [19]. $T_N = 200 \pm 0.5$ K is the magnetic ordering temperature. The dependencies for $Gd_{0.65}Y_{0.35}$, $Gd_{0.66}Y_{0.34}$, and $Gd_{0.69}Y_{0.31}$ almost coincide on this scale. Dotted rectangle corresponds to Fig. 2(b). (b) Temperature dependencies of the specific heat $c_p(T)$ in the vicinity of T_1 for $Gd_{0.69}Y_{0.31}$ ($H = 0$, solid squares), $Gd_{0.66}Y_{0.34}$ (circles, solid for $H = 0$ and open for $H = 5$ kOe, shifted vertically for clarity), and $Gd_{0.65}Y_{0.35}$ (triangles, solid for $H = 0$ and open for $H = 5$ KOe, shifted vertically for clarity). Lines are guides for the eye. Arrows mark T_1, the temperature of the helical antiferromagnet–ferromagnet transition. PM: paramagnetic; HAFM: helical antiferromagnetic; FM: ferromagnetic phases.

Subtracting the $c_p(T)$ dependence for the reference object, ferromagnetic $Gd_{0.69}Y_{0.31}$, from dependencies for $Gd_{0.65}Y_{0.35}$ and $Gd_{0.66}Y_{0.34}$ we obtain the resulting $\Delta c_p(T)$ dependencies, presented in Fig. 3. Interpolation of $Gd_{0.69}Y_{0.31}$ $c_p(T)$ dependence for the subtraction was performed employing linear least-square fit within ± 5 K from the required temperature; dependencies for $Gd_{0.65}Y_{0.35}$ and $Gd_{0.66}Y_{0.34}$ were used without any preprocessing. We also present a fragment of the dependence for $Gd_{0.65}Y_{0.35}$ in the magnetic field $H = 5$ kOe that suppresses the magnetic transition at T_1. The presence

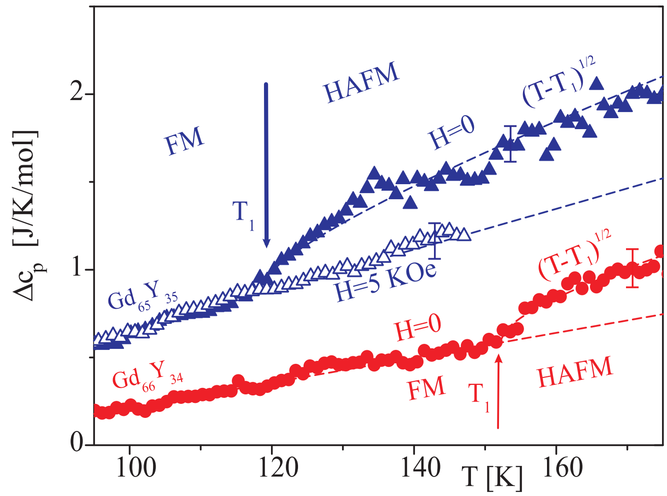

FIG. 3. Temperature dependencies of the specific heat $\Delta c_p(T)$ for $Gd_{0.65}Y_{0.35}$ at $H = 0$ (solid triangles) and $H = 5$ kOe (open triangles, magnetic transition suppressed), and $Gd_{0.66}Y_{0.34}$ (solid circles) after subtracting the dependence for the reference $Gd_{0.69}Y_{0.31}$. Error bars are reported by the calorimeter. Dashed lines stay for the linear background dependencies and for the square-root fits associated with the presumed second-and-a-half–order transition, suggested to arise from the underlying Lifshitz transition. T_1 are the temperatures of this transition, obtained from the square-root fits. HAFM: helical antiferromagnetic; FM: ferromagnetic phases.

of the anomaly at $H = 0$ and its absence at $H = 5$ kOe prove that the observed anomaly is really associated with the studied transition.

IV. DISCUSSION

The anomaly associated with the transition is clearly resolved, and both the samples behave in a similar way. It is worth mentioning that the very shape of the anomaly at $H = 0$, even without physical background, is sufficient to identify this transition as an Ehrenfest second-and-a-half–order. Indeed, the Ehrenfest order of transition is higher than two, because the additional specific heat at $T \to T_1$ tends to zero, in contrast with the ordinary second-order behavior, Fig. 1(a). On the other hand, the clearly nonlinear and up-arched anomaly corresponds to the order of transition lower than three. The square-root dependence predicted for the second-and-a-half–order transition fits reasonably the $\Delta c_p(T)$ dependencies for both the samples, in agreement with the expectations, Fig. 1(b). Hence we conclude that the studied phase transition at T_1 is likely a second-and-a-half–order transition according to the Ehrenfest classification.

The relation of such a behavior with the underlying Lifshitz transition, the only known second-and-a-half–order transition so far, seems highly likely. On the other hand, the studied transition is definitely not a "genuine" Lifshitz transition described in [1] but presumably a complex combination of Lifshitz transition and magnetic phase transition (see above). Moreover, the role of magnetoelastic phenomena is also important [33] and cannot be neglected. Therefore, the studied transition is apparently a product of the interplay of conductive, magnetic, and elastic subsystems in the vicinity of

Lifshitz transition. A reasonable suggestion is that this complex transition preserves nevertheless the square-root anomaly in the specific heat characteristic of the genuine Lifshitz transition. The alternative is an assumption that the observed anomaly is not related with the Lifshitz transition at all and arises from some other phenomenon, which seems unlikely as no such alternate phenomena are known. Of course, these preliminary suggestions require theoretical consideration. Probably the recent progress in the *ab initio* calculations [28] would provide the full description of this combined Lifshitz-and-magnetic transition.

The probable alternative scenarios should also be considered. The approach that does not involve Lifshitz transition should examine temperature-dependent energies of the two competing magnetic phases, helical and ferromagnetic, under the most general assumptions but without employing specific relations characteristic of the Lifshitz transition. This problem is destined for the phenomenological Landau analysis, which has been performed in [38] with special interest to the GdY system. It revealed that the studied transition should be second order (while introduced hexagonal in-plane magnetic anisotropy makes it even first order). Therefore, we conclude that the observed non-second-order behavior arises from some extra phenomenon, and all the features point to the Lifshitz transition.

V. CONCLUSION

In summary, we find that the "order-order" magnetic phase transition in temperature in the GdY system is associated with an exotic specific heat anomaly that identifies this transition as an Ehrenfest second-and-a-half–order. Here, Ehrenfest's second-and-a-half–order transition was directly observed as a specific heat anomaly. There are plausible reasons to associate this anomaly with the underlying Lifshitz transition.

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