(kT ∿ 0.4 meV at 4.2°K) makes no significant contribution to the broadening of the exciton-absorption lines, as proposed earlier [1]. Apparently, just as in the case of shallow impurities, the half-width of an exciton-absorption line is determined at low temperatures by the interaction of the excitons with the zero-point vibrations of the crystal lattice. Estimates based on the theory of [9] yield $\Delta h\nu \sim 0.01 \pm 0.02$ meV. At the same time the concentration averaged over the crystal volume reached $\sim 10^{13}$ cm$^{-3}$ in our experiments[1]. A noticeable contribution to the line broadening can be made by interactions of the excitons with one another [2].

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# ANOMALOUS BEHAVIOR OF THE MAGNETIC SUSCEPTIBILITY NEAR THE MAGNETIC-COMPENSATION POINT IN COMPOUNDS OF RARE-EARTH METALS WITH IRON

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In ferrimagnetic compounds of rare-earth metals with iron ($HoFe_3$, $ErFe_3$, and $ErFe_2$) we observed, near the compensation point $T_c$, maxima on the temperature dependence of the differential susceptibility $\chi$, one at $T < T_c$ and another at $T > T_c$. Calculations of $\chi$ performed on the basis of the molecular-field theory have shown that such maxima on the $\chi(T)$ curves should appear in the noncollinear phase in fields weaker than the effective exchange field, if the magnetic field is directed along the easy-magnetization axis. It is shown that the theoretical value of the susceptibility in the noncollinear phase agrees with the experimental data.

In ferrimagnetic compounds of rare earth metals with iron, $ErFe_2$, $ErFe_3$, and $HoFe_3$, near the magnetic compensation temperature (490, 250, and 393°K,

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[1] The volume lifetime of the excitons in the investigated "ultrapure" germanium samples, at the same exciton concentration and at 4.2°K, amounts to 5 - 10 μsec according to the data of B.V. Zubov and V.P. Kalinushkin (private communiation).

respectively), the differential susceptibility exhibits anomalies (Fig. 1). In fields weaker than 1.5 kOe, the $\chi(T)$ curve has a minimum at $T_c$, but with increasing magnetic field the behavior of the susceptibility becomes more complicated: two maxima appear on the $\chi(T)$ curves of $HoFe_3$ and $ErFe_3$, one at $T < T_c$ and the other at $T > T_c$. The samples were prepared in the laboratory of E.M. Savitskii by the technology described in [1].

These compounds are two-sublattice ferrimagnets. It is known [2, 3] that an induced angular structure is produced in ferrimagnets in relatively weak fields near the compensation temperature. We shall show that the observed anomalies can be due to transitions from the collinear to the angular phase.

In $RFe_2$ and $RFe_3$ compounds [5, 4], just as in rare-earth iron garnets [6], the exchange interaction between the rare-earth ions is weak and can be neglected, whereas a strong exchange interaction exists in the iron sublattice. On this basis, the following model can be used to describe the magnetic properties of these ferrimagnets. The iron-ion sublattice is in a saturated state (the paraprocess can be neglected), and the magnetic ordering of the rare-earth sublattice is determined by the exchange field exerted by the iron sublattice.

The main features of the behavior of the susceptibility can be explained, with a uniaxial ferrimagnet as an example, for two directions of the magnetic field H, parallel and perpendicular to the easy axis (EA).

To calculate the susceptibility $\chi = -a^2\phi/dH^2$ we use the thermodynamic potential for H $\parallel$ EA in the form [7]:

$$\phi = -HM_1\cos\theta - \int_0^{H_{eff}} M_2(h)\,dh - K\cos^2\theta\,, \qquad (1)$$

where $H_{eff}^2 = H^2 + (\lambda M_1)^2 - 2\lambda M_1 H\cos\theta$, $\theta$ is the angle between the external field H and the magnetic moment $M_1$ of the iron sublattice, K is the crystal anisotropy constant, $M_2(h)$ is the magnetization of the rare-earth sublattice as a function of the molecular field, and $\lambda M_1$ is the exchange field exerted by the iron sublattice on the rare-earth sublattice.

Calculations yield the following expressions for the susceptibility:

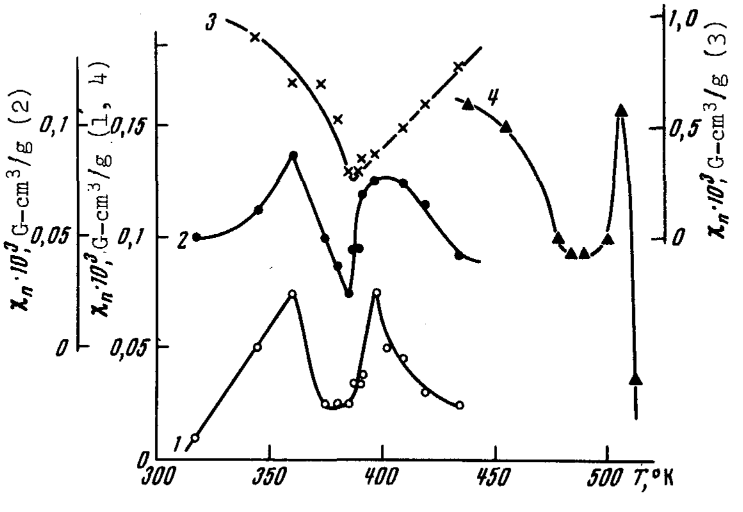

Fig. 1. Temperature dependence of the differential magnetic susceptibility $\chi$ of $HoFe_3$ in fields 11 kOe (curve 1), 9 kOe (2), and 1.5 kOe (3), and of $ErFe_2$ in a field 11 kOe.

a) in the collinear phase

$$\chi = \frac{N\mu_0^2}{kT}\,\frac{dB_J(x)}{dx},$$

$$x = \begin{cases} \dfrac{\mu_0(\lambda M_1 + H)}{kT}, & T < T_K \\[2ex] \dfrac{\mu_0(\lambda M_1 - H)}{kT}, & T > T_K \quad \text{и} \quad H < \lambda M_1, \end{cases} \tag{2}$$

where $\mu_0$ is the magnetic moment of the rare-earth ion at T = 0°K, N is the number of rare-earth ions per unit volume, and $B_J(x)$ is the Brillouin function;

b) in the noncollinear phase

$$\chi = \frac{1}{\lambda}\left[1 + \frac{2K\lambda}{H^2}\cos^2\theta + \left(\frac{4K\lambda}{H}\cos\theta - \frac{2K}{M_1}\right)\sin\theta\,\frac{\partial\theta}{\partial H}\right], \tag{3}$$

where $\theta(T, H)$ is determined from the equation $\partial\phi/\partial\theta = 0$.

If the field H is perpendicular to the magnetization EA, then the sign of the anisotropy constant K should be reversed in formulas (1) and (3), in analogy with the case of the magnetization difficult axis (DA).

In the field range of greatest interest, $2K/M_1 \ll H \ll \lambda M_1$, the expressions for $\chi$ assume simpler forms

$$\chi_{\parallel \mathrm{EA}} = \frac{1}{\lambda}\left[1 + \frac{2K\lambda}{H^2}(1 + 2\xi)\cos^2\theta\right],$$

$$\chi_{\parallel \mathrm{DA}} = \frac{1}{\lambda}\left[1 - \frac{2K\lambda}{H^2}\left(1 + \frac{2}{\xi}\right)\cos^2\theta\right],$$

where

$$\xi = \frac{1 + 2K\lambda/H^2(1-\delta)}{1 - 2K\lambda/H^2(1-\delta)}, \qquad \delta = \lambda\frac{\partial M_2}{\partial H_{\mathrm{eff}}} < 1, \tag{6}$$

and $\cos\theta(H, T)$ is determined from the equation $\partial\phi/\partial\theta = 0$.

If H ∥ EA, a noncollinear phase exists when

$$H > H_{\mathrm{cr}} = \sqrt{2K\lambda/(1-\delta)}. \tag{7}$$

The temperature dependence of $\chi(T)$ at equal values of the field $H > H_{\mathrm{cr}}$, for both H ∥ EA and H ∥ DA, is determined from (4) and (5) and is shown in Fig. 2.

It follows from (4), (5), and (6) that when the field is increased ($H > H_{\mathrm{cr}}$) (in which case the

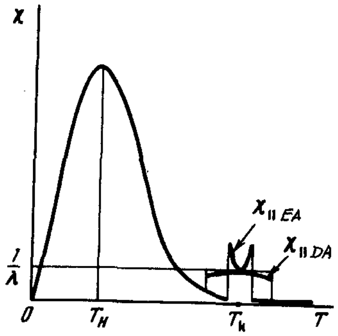

Fig. 2. Theoretically calculated temperature dependence of the differential magnetic susceptibility: $\chi_{\mathrm{EA}}$ and $\chi_{\mathrm{DA}}$ - magnetic field directed along the easy and difficult magnetization axes, respectively.

temperature region in which the angular phase exists increases), the susceptibility peaks and dips indicated in Fig. 2 near the magnetic-compensation points decrease, and only the jump remains. It should be noted that the peaks and dips on the plots of the susceptibility against the temperature appear only when the anisotropy is taken into account. In the isotropic model we have in the angular phase $\chi(T) = 1/\lambda$.

Obviously, the behavior of the susceptibility in a polycrystal is more complicated but its main features undoubtedly remain the same.

To verify the extent to which the above-described theoretical model agrees with experiment, we present a few estimates. When $T_c$ is approached, the coercive force increases like $H_c = 2K/M_s$ [8]. From this and from our experimental data (see also [1]), it follows that the magnetic-anisotropy constants of $ErFe_2$, $ErFe_3$, and $HoFe_3$ near $T_c$ are respectively $1 \times 10^3$, $3 \times 10^3$, and $3 \times 10^3$ erg/cm$^3$. The molecular-field constant $\lambda$ can be determined from the formula

$$\lambda = \frac{2S}{gJ}\,\frac{H_{e2}}{M_1},$$

where $M_1$ is the magnetization per unit volume, and $H_{e2}$ is the effective exchange field determined from the temperature dependence of the magnetization of the rare-earth sublattice by the method proposed in [9]. For the compounds $ErFe_2$, $ErFe_3$, and $HoFe_3$, the values of $\lambda$ are $2.7 \times 10^3$, $0.8 \times 10^3$, and $0.9 \times 10^3$, respectively. $H_{cr}$ calculated from formulas (6) and (7) for these compounds is approximately equal to 2 - 3 kOe. This shows that an angular structure was indeed realized in the fields used in the experiment. The theoretically-predicted form of the $\chi(T)$ plots in the noncollinear phase agrees qualitatively with experiment. In addition, the experimental values of the susceptibility at $T = T_c$, corresponding to the angular phase, are in fair agreement with the value $\chi = 1/\lambda$ that follows from the theory. Thus, $\chi(T_c) = 0.12 \times 10^{-3}$, $0.09 \times 10^{-3}$, and $0.025 \times 10^{-3}$ G-cm$^3$/g-Oe for $ErFe_3$, $ErFe_2$, and $HoFe_3$, respectively, as against $\chi = 1/\lambda = 0.14 \times 10^{-3}$.

Thus, our investigation demonstrates that an angular structure is produced in $ErFe_2$, $ErFe_3$, and $HoFe_3$ near the compensation temperature in a relatively weak magnetic field ($H \gtrsim 2 - 3$ kOe). To investigate the resultant angular magnetic structure it is useful to study the anomalies of other physical quantities such as the magnetocaloric effect, galvanomagnetic phenomena, and the speed of sound.

In conclusion, we are grateful to Professor K.P. Belov for taking part in a discussion of the results, and to V.F. Terekhova and V.E. Kolesnichenko for preparing the samples.

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# MANIFESTATION OF CRYSTAL STRUCTURE SINGULARITIES IN THE IR SPECTRA OF GERMANIUM DICHALCOGENIDES

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We report the first investigations of the spectra of $GeS_2$ and $GeSe_2$ in the far infrared, where we observed, in addition to the ordinary vibrational bands, also absorption bands similar to those seen in the spectra of molecular crystals.

One of the direct methods of studying the structure of a substance is to analyze its IR spectrum in the region where the crystal lattice absorption bands are located. To interpret the results, however, it is necessary to study as large a number of IR spectra of similar compounds as possible. Such compounds are the families of the mono- and dichalcogenides of germanium.

We have investigated, for the first time, the IR spectra of powders of crystals of these compounds in the region from 700 to 33 $cm^{-1}$, where their vibrational absorption spectra are located. The crystals were grown in quartz ampules from melts of suitable batches of Ge with S or Se. The spectra were studied with the UR-10 and FIS-3 analyzers. The crystal powders were pressed in hot polyethylene.

According to their x-ray structure analysis, GeS and GeSe are isostructural and crystallize in a rhombic lattice of space group $D_{2h}^{16}$ - Pcmn [1]. In such a structure, the valently bound atoms of different kinds form double layers, and each atom is surrounded by neighbors of the other kind forming a strongly distorted octahedron. In "their own" double layer, the Ge atoms have three nearest and two more remote neighbors; the farthest neighbor lies in the next layer. The bonds between atoms of different sorts inside the double layer have an ion-covalent character, whereas the bond between neighboring layers is greatly weakened.

The IR transmission spectra of GeS and GeSe (Fig. 1) have a complicated absorption band and are practically identical in form, although in GeSe the entire band is regularly shifted to the long-wave region of the spectrum. Since this shift is due to the replacement of the S atom in the lattice by the heavier Se, it can be assumed that the monochalcogenides of germanium are indeed isostructural [1].

X-ray structure investigations of $GeS_2$ and $GeSe_2$ have shown that they crystallize in a rhombic lattice with space group $D_{2h}^{13}$ - Pmmn, i.e., they are isostructural [2, 3]. Their structure is in fact a strongly deformed structure of the $CdI_2$ type. The latter is made up of two-dimensional platelets of octahedral groups of $CdI_6$, resulting in the formation of layers of the metal atoms (A), which produce the metric basis of the crystal lattice and are

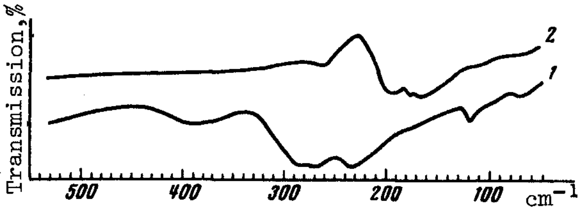

Fig. 1. IR transmission spectra of germanium monochalcogenides: 1 - GeS, 2 - GeSe.