formation (9). It follows therefore that in the sum that represents δE_{VV} a nonzero contribution is made only by intermediate states that are even in π. The calculation of this sum calls for knowledge of all the excited states of the molecule, and is a difficult quantum-chemistry problem. In any case $|\chi_M|$ should apparently exceed $|2\chi_x|$. The inequality (1) then restricts quite strongly the possible value of χ_M.

Thus, the diamagnetic susceptibility of a molecule does not differ greatly from double the exciton susceptibility, even though the trial function (14) does not contain the wave functions of two excitons. It should be noted that the accuracy of the obtained inequality corresponds to the accuracy of the trial wave function (14).

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Antiferromagnetic resonance in hematite with Sn^{4+} impurity

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Antiferromagnetic resonance is studied in single crystals of α-Fe_2O_3 + 0.8 wt% Sn^{4+} over the temperature interval 1.2 to 300 K and the frequency range 23 to 70 GHz. It is found that the Morin point, if it exists, lies below 1.2 K. The temperature dependence of the parameters that determine the AFMR spectrum is investigated. It is found that the isotropic gap in the AFMR spectrum and the hexagonal anisotropy in the basal plane increase anomalously with lowering of the temperature. On cooling of the crystal in a magnetic field $H_0 \perp D_3$, there freezes into it at $T < 18 \pm 1$ K a uniaxial anisotropy with easy direction of the ferromagnetic vector $\mathbf{m}_0 \parallel \mathbf{H}_0$. A theoretical investigation is made of a mechanism based on the formation of bound states Fe^{2+}–Sn^{4+}, which lead, because of distortion of the local crystalline field on the Fe^{2+} ions, to the inducing of additional anisotropy in the crystal. It is shown that this mechanism describes all the observed effects.

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Hematite, α-Fe_2O_3, is a well studied antiferromagnetic material with $T_N = 970$ K. It is known that at temperature $T_M = 263$ K (the Morin point), a phase transition occurs in hematite, from an easy-plane weakly ferromagnetic state at $T > T_M$ to an easy-axis antiferromagnetic state at $T < T_M$. Investigations of the static magnetic properties,[1] of the Mössbauer effect,[2] and of neutron diffraction[3] have shown that upon introduction into hematite of small quantities (~1%) of metallic impurity (Al, Ti, Sn, etc.), the Morin point changes. It follows from these researches that the greatest effect on the Morin point is caused by introduction into hematite of tetravalent tin.

The present paper is devoted to a study of antiferromagnetic resonance (AFMR) over a broad temperature range in hematite that contained 0.8 wt% Sn^{4+}. As an NMR study has shown,[4] in this case the Morin point is substantially lowered: $T_M < 77$ K. The AFMR method was chosen because it is very sensitive to change of the magnetic structure and enables one to determine a number of magnetic constants.

METHOD AND SPECIMENS

AFMR in hematite was studied on a direct-amplification magnetic spectrometer. A shorted waveguide served as the measurement cell; the specimen was placed on its copper cap, at an antinode of the microwave magnetic field. In order that elastic stresses should not occur in the specimen on cooling, it was not cemented to the waveguide cap but was lightly attached to it with a stopper of foam plastic. The resonance absorption line was recorded with an xy recorder, which registered the change of the microwave signal reflected from the crystal as a function of the value of the magnetic field H. The magnetic field was produced by a laboratory electromagnet and was measured with a Hall detector with accuracy 1%.

The measurements were made over the frequency range 23 to 70 GHz and over the temperature interval 1.2 to 300 K. Temperatures below 4.2 K were obtained by evaporation of liquid helium; above, by use of a vacuum cryostat similar to that described in Ref. 5.

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The temperature was measured with a semiconductor thermometer. The accuracy of measurement and maintenance of the temperature was no worse than 1%.

Monocrystals of α-$Fe_2O_3 + Sn^{4+}$ were grown from solution in the melt, by a method similar to that described in Ref. 6, by R. A. Voskanyan, in the Institute of Crystallography of the Academy of Sciences, USSR. The specimens were black-colored plates with a mirror-metallic brilliance, of dimensions ~5×3×0.3 mm^3. The Sn^{4+} impurity content was determined with an x-ray microanalyzer.

EXPERIMENTAL RESULTS

Mounting the specimen so that the magnetic field **H** was parallel to the basal plane of the crystal, we observed the resonance absorption line. Investigations showed that the resonance field H_R depends on the temperature and on the direction of the magnetic field in the basal plane of the crystal–on the azimuthal angle φ_H. Figure 1 shows the results of measurements at various temperatures at fixed φ_H. Figure 2 shows the variation of the resonance field with φ_H at $T = 4.2$ K. It follows from these measurements that over the whole temperature interval investigated, 1.2 to 300 K, the AFMR spectrum of α-$Fe_2O_3 + Sn^{4+}$ is described by the usual expression for an easy-plane antiferromagnet[7,8]:

$$(\nu/\gamma)^2 = H(H+H_D) + H_\Delta^2 + H_6^2 \cos 6\varphi_H, \tag{1}$$

where $\gamma = 2.8$ GHz/kOe is the gyromagnetic ratio, H_D is the Dzyaloshinskiĭ field, and H_Δ^2 and H_6^2 are, respectively, the isotropic and anisotropic gaps in the AFMR spectrum.

By processing the experimental data on a computer by the method of least squares, we determined the values of the parameters that occur in (1), at various temperatures. The value of H_D decreases insignificantly with lowering of temperature; it is 23.6 kOe at 293 K, 23.4 kOe at 77 K, and 22.8 kOe at 4.2 K. The error in the determination of H_D was ~0.3 kOe. These values are close to the value $H_D = 22$ kOe obtained in Ref. 9 on pure hematite. The values of H_Δ^2 and H_6^2 as functions of temperature are shown in Figs. 3 and 4, respectively. Our values at room temperature, $H_\Delta^2 = 13.6 \pm 0.5$ kOe^2 and $H_6^2 = 0$, coincide, within the limits of experimental accuracy, with those given in Ref. 9 for pure hematite.

It was observed that on cooling of the specimen in a magnetic field H_0, there "freezes" into the crystal at 180° anisotropy in the basal plane, with the easy direction of the weak ferromagnetic moment parallel to H_0. The influence of this anisotropy on the AFMR spectrum can be taken into account by introducing on the right side of (1) an additional term $H_2^2 \cos 2(\varphi_H - \varphi_{H_0})$. Within the limits of experimental accuracy, the value of H_2^2 was independent of the direction of the field H_0 in which the specimen was cooled, provided $H_0 > 0.5$ kOe, and of the temperature T_0 with which the cooling in the field began, provided $T_0 > 30$ K. The variation of H_2^2 with temperature, determined under these conditions, is shown in Fig. 5. It is seen that H_2^2 decreases sharply with rise of temperature. The "freezing" temperature of the 180° anisotropy, i.e. the temperature below which it appears, is 18 ± 1 K. The values of the parameters H_Δ^2 and H_6^2 for cooling of the specimen in a field and without a field coincided, within the limits of experimental accuracy.

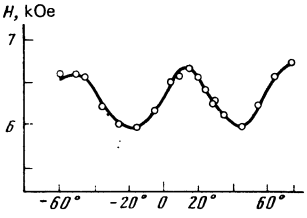

FIG. 2. Variation of resonance field with azimuthal angle φ_H; $T = 4.2$ K.

DISCUSSION OF RESULTS

From the fact that the AFMR spectrum is described by formula (1), it follows that over the whole range of temperature investigated, α-Fe_2O_3 + 0.8 wt% Sn^{4+} is an easy-plane antiferromagnetic with weak ferromagnetism. Thus the Morin point, if it exists, lies below 1.2 K. In the contrary case, if the magnetic structure changed to easy-axis, there would appear in the spin-wave spectrum a gap $\nu_0 = \gamma\sqrt{2H_A H_E}$. Since the exchange field in Hematite is large, $H_E = 9200$ kOe, the frequency ν_0 is above 100 GHz except within a quite narrow neighborhood of the Morin point, where A_A passes through zero. In this connection it is pertinent to mention that in Ref. 4, done on crystals of hematite with the same tin content 0.8 wt%, an appreciable decrease of the weak ferromagnetic moment σ is noted at $T < 77$ K: σ(4.2 K) is 70% of σ(293 K). This effect was explained in Ref. 4 by a transition of a part of the crystal volume–larger, the lower the temperature—to an easy-axis state. The assumed presence of two types of domain in the specimen, corresponding to two directions of the sublattice magnetizations (along the

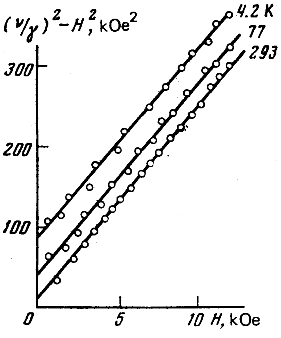

FIG. 1. AFMR spectrum of α-Fe_2O_3 at various temperatures.

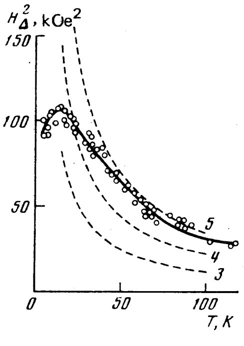

FIG. 3. Temperature dependence of the isotropic gap H_Δ^2 in the AFMR spectrum. The dotted curves are values calculated by formula (10), $H_{\Delta\,\text{theor}}^2$. The numbers on the dotted curves are values of the parameter e_0/k.

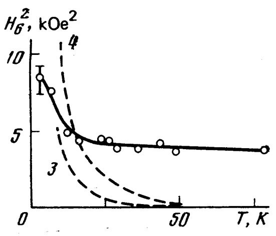

FIG. 4. Temperature dependence of the anisotropic gap H_6^2 in the AMFR spectrum. The dotted curves are values calculated by formula (11), $H_{6\,\text{theor}}^2$. The numbers on the dotted curves are values of the parameter e_0/k.

axis, $\theta=0$, and in the plane, $\theta=\pi/2$), would produce, first, a decrease of the resonance susceptibility χ'' in proportion to the decrease of the number of spins with an easy-plane orientation, and, second, a broadening of the resonance line because of the spins of the domain walls, whose directions correspond to intermediate values $0<\theta<\pi/2$. In our experiments, such a change of shape of the resonance line with lowering of the temperature was not noted; this apparently excludes the possibility of nonuniform magnetization of the crystal. Probably the reason for the discrepancy can be explained by the fact that in Ref. 4 magnetometer measurements were made of the ferromagnetic moment of a prism of several crystals, superposed one upon another, and among them might be crystals with a higher Morin point.

The nature of the appreciable change of the Morin point observed by us upon introduction of a relatively small quantity of Sn^{4+} impurity is explained by the appearance in the specimen of charge-compensating Fe^{2+} ions. Such a possibility was first discussed in Ref. 10, and later Fe^{2+} ions in hematite with tin impurity were detected experimentally by means of the Mössbauer effect.[2] As is well known, the magnetic anisotropy in hematite consists of two parts of different origin: the dipole-dipole and single-ion anisotropies, with easy direction of the spins in the plane and along the D_3 axis, respectively. Accordingly, the second-order anisotropy constant of hematite is the sum of constants corresponding to these parts, and of different signs:

$$a=a_d+a_{si}.$$

In hematite, the constants a_d and a_{si} differ little in absolute value (at $T=4.2$ K, $|a_d+a_{si}|/a_d\approx 2\%$[11]); therefore the difference in the temperature variations of a_d and a_{si} leads to a change of sign of a, and consequently of the easy spin direction, at a certain temperature $T=T_M$ (here we neglect the effect on T_M of the higher-order anisotropy constants,[12] which is not important in the case considered). Hence it is evident that a small change of the single-ion anisotropy is sufficient for substantial change of a, and consequently of T_M. This is what occurs when Fe^{2+} ions appear in the crystal. As is well known, this ion, in an octahedral position corresponding to the hematite lattice, has a threefold orbitally degenerate ground state. The existence of trigonal distortion of the symmetry of the local field apparently does not remove the degeneracy completely, and therefore there corresponds to the Fe^{2+} ion a nonzero orbital moment and a strong spin-orbit interaction. As a result, the single-ion anisotropy is much larger for an Fe^{2+} ion than for an Fe^{3+}, since it is larger, the stronger the spin-orbit interaction, and since Fe^{3+} is in an S state. If, as is usual, we suppose that the anisotropy is additive with respect to the spins present in a sublattice, then it is clear that a small admixture of Fe^{2+} ions can noticeably affect the anisotropy of the crystal. The presence of Fe^{2+} ions also determines other effects that we observed: an anomalous increase of the isotropic part of the gap H_Δ^2 with lowering of temperature, and also a sharp increase of the hexagonal anisotropy and occurrence of frozen-in anisotropy at low temperatures. That these effects have the same character is apparently indicated by the fact that in the temperature variations of the constants H_Δ^2, H_6^2, and H_2^2 (see Figs. 3, 4, and 5), singularities are observed at the same temperature $T\sim 20$ K.

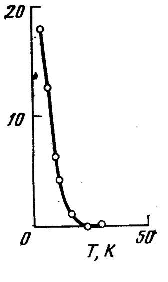

FIG. 5. Temperature dependence of the value of the frozen-in anisotropy H_2^2.

We shall first consider the mechanism that leads to the occurrence of frozen-in anisotropy. The presence in one crystal of different magnetic ions should in principle always lead to the occurrence of frozen-in anisotropy. This occurs most simply if there are in the crystal nonequivalent positions of magnetic ions. Since the local axes of anisotropy are in general differently directed in nonequivalent positions, in an external magnetic field different distributions of the magnetic ions over these positions will correspond to different magnetic energies of the whole specimen; and at high temperatures, when diffusion of ions through the specimen is possible, a distribution will be established that corresponds to minimum energy. If we now cool the specimen, the distribution of ions that has established itself cannot change, and it will make a contribution to the anisotropy of the specimen. In a case in which the magnetic ions differ only in valence, for example as in our case of Fe^{2+} and Fe^{3+}, a change of the spatial distribution is possible without diffusion of the ions, by electronic jumps of the type

$$Fe^{2+}\rightleftharpoons Fe^{3+}.$$

The temperature of freezing-in of the anisotropy is then considerably lower, of the order of tens of Kelvins, since the activation energy of the process of electronic jumps is smaller than that of the process of ion diffusion. In the case of hematite, it is true, all cation positions are equivalent; but freezing in of the anisotropy can take place, for example, because of the formation of $Fe^{2+}-Fe^{2+}$ pairs and because of distortion of the local symmetry of the crystalline field on Fe^{2+} ions in positions adjacent to Sn^{4+} ions. For an answer to the question, what the nature is of the frozen-in anisotropy, it would be useful to investigate its dependence on the impurity concentration; but unfortunately, we had at our disposal only crystals with a single impurity content. Nevertheless it was found that the second mechanism could explain not only the inducing of the anisotropy, but also other observed effects.

We shall consider what occurs on introduction of Sn^{4+} ions into hematite. As has already been stated, for preservation of the electrical neutrality of the crystal, some of the Fe^{3+} ions are reduced to Fe^{2+}; the number of Sn^{4+} and Fe^{2+} ions is the same. It must at the same time be taken into account that the Sn^{4+} and Fe^{2+} ions are bound to each other by electrostatic forces; therefore the formation of bound states of Sn^{4+} and Fe^{2+} ions, $Sn^{4+}-Fe^{2+}$ pairs, is energetically advantageous. The energy of dissociation $E_{\rm diss}$ of such a pair in hematite is unknown to us; but in oxides of other elements, for example NiO with Li impurity,[13], it has been measured, and the temperature $T_{\rm diss}$ corresponding to this energy is of the order of hundreds of Kelvins. Thus at a low temperature $T \ll T_{\rm diss}$, it may be supposed that practically all the Sn^{4+} and Fe^{2+} ions in the crystal are in a bound state. Figure 6 shows schematically one of the Sn^{4+} ions and the six cation positions nearest to it, in a projection on the basal plane. From what was said above and from the smallness of the concentration of the tin impurity $x = 0.52 \cdot 10^{-2}$ (x is the ratio of the number of tin ions to the number of iron ions), it follows that one of the nearest positions is occupied by Fe^{2+} ions and the rest by Fe^{3+} ions. The difference of the electronic shells of the Sn^{4+} ions from the Fe ion leads to an axial distortion of the crystalline field on the Fe ions in the adjacent positions, and this in turn, in the single-ion approximation, leads to the appearance on these ions of a uniaxial magnetic anisotropy, with the anisotropy axis parallel to the vector **R** that connects the given iron ion with the tin ion. Since the single-ion anisotropy is appreciably larger for the Fe^{2+} ion than for the Fe^{3+}, we may neglect the latter and write the anisotropy energy of a single $Sn^{4+}-Fe^{2+}$ pair in the form

$$e_a = -e_0 \cos^2 \varphi, \tag{2}$$

where φ is the angle between the spin of the Fe^{2+} ion and the vector $\mathbf{R}_{Fe^{2+}}$. Since the spins of all the iron ions are coupled by strong exchange interaction and are parallel to the antiferromagnetism vector **l**, the six possible positions of the Fe^{2+} ion correspond to three values of e_a:

$$e_{aj} = -e_0 \cos^2(\varphi_l + j\pi/3), \tag{3}$$

where $j = 0, 1, 2$, and where the angle φ_l is measured from a binary surface.

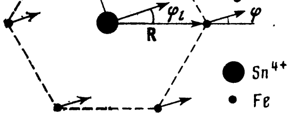

FIG. 6. Schematic representation of an Sn^{4+} ion and the cation positions nearest to it, in a projection on the basal plane.

Accordingly, the contribution to the anisotropy energy of the crystal from all $Sn^{4+}-Fe^{2+}$ pairs is

$$E_a = -e_0 \sum_{j=0}^{2} N_j \cos^2(\varphi_l + j\pi/3), \tag{4}$$

where N_j are the occupation numbers of the respective positions.

At a sufficiently high temperature, when the mobility of the Fe^{2+} ion, determined by the process $Fe^{2+} \rightleftarrows Fe^{3+}$, is sufficiently high, during the time of the experiment there is established in the crystal an equilibrium distribution of the Fe^{2+} ions over these positions corresponding to the direction of the vector **l** that has been established (the angle φ_{l0}). Then the occupation numbers are determined by Boltzmann statistics:

$$N_j = N \exp\left[-\frac{e_{aj}(\varphi_{l0})}{kT}\right] \Big/ \sum_{j=0}^{2} \exp\left[-\frac{e_{aj}(\varphi_{l0})}{kT}\right], \tag{5}$$

where N is the number of $Sn^{4+}-Fe^{2+}$ pairs.

As will be shown later, in the temperature range of interest to us the condition $e_0 \ll 2kT$ is satisfied. In this case, the expression (4), with use of (5), can be expanded in powers of e_0/kT. Retaining in the expansion only terms dependent on φ_l and of no higher than second order in e_0/kT, we get

$$E_a = -\frac{e_0^2 N}{8kT}\left\{\cos 2(\varphi_l - \varphi_{l0}) + \frac{e_0}{8kT}\cos[6\varphi_{l0} + 2(\varphi_l - \varphi_{l0})]\right\}. \tag{6}$$

The expression (6) can, without loss of accuracy, be still further simplified:

$$E_a = -\frac{e_0^2 N}{8kT}\left(1 + \frac{e_0}{8kT}\cos 6\varphi_{l0}\right)\cos 2(\varphi_l - \varphi_{l0}). \tag{7}$$

From (7) it is seen that the mechanism under consideration leads to the induction in the basal plane of the crystal of a uniaxial anisotropy, for which the easy direction of the antiferromagnetic vector **l** coincides, to within terms linear in e_0/kT, with the direction $\mathbf{l}_0$—which, as usual, makes with the magnetic field **H** an angle that differs from $\pi/2$ by a quantity δ, small in proportion to the ratio of the anisotropy energy in the basal plane to the Zeeman energy. Calculations show that

$$\delta = \frac{3e_0^3 BN \sin 6\varphi_H}{32(kT)^2 H(H + H_D)}.$$

Under the conditions of our experiment, the quantity δ is small, and therefore we may suppose that $\mathbf{l}_0 \perp \mathbf{H}$.

The induced anisotropy differs from the usual anisotropy in that during a rotation of the magnetic field **H** in the basal plane, slow in comparison with the time for the electronic jump $Fe^{2+} \rightleftarrows Fe^{3+}$, the easy direction of the induced anisotropy rotates together with **H**, and the crystal is always at the minimum of E_a. But for the spin oscillations corresponding to AFMR, the induced anisotropy does not differ from the usual, since the easy direction cannot change with the AFMR frequency $\sim 10^{10}$ Hz.

The thermodynamic potential of an antiferromagnet with the hematite structure, through terms quadratic in **l** and **m** and with allowance for the induced anisotropy (7), has the form

$$\Phi=\frac{B}{2}m^2+\frac{a}{2}l_z^2+d(l_xm_y-l_ym_x)-\frac{e_0^2N}{8kT}\left(1+\frac{e_0}{8kT}\cos 6\varphi_{l_0}\right)\times\cos 2(\varphi_l-\varphi_{l_0})-\mathbf{mH}. \qquad (8)$$

By starting from (8) and solving the Landau-Lifshitz equation, one can easily obtain the expression for the low-frequency branch of the AFMR spectrum:

$$\left(\frac{\nu}{\gamma}\right)^2=H(H+H_D)+\frac{e_0NB}{2kT}\left(1+\frac{e_0}{8kT}\cos 6\varphi_{l_0}\right), \qquad (9)$$

where, as usual, $H_D=dl_0$ and $H_B=Bl_0/2$.

It is evident from (9) that introduction of impurity Sn^{4+} into hematite leads to the appearance in the AFMR spectrum of isotropic and anisotropic gaps,

$$H^2_{\Delta\text{theor}}=e_0^2NB/2kT, \qquad (10)$$

and

$$H^2_{6\text{theor}}=e_0^3NB/16(kT)^2, \qquad (11)$$

respectively, in which only the single parameter e_0 remains unknown.

We shall now consider another case, when the temperature is low and when the mobility of the Fe^{2+} ion, determined by the process $Fe^{2+}\rightleftarrows Fe^{3+}$, is so small that during the time of the experiment no change occurs in the distribution of the Fe^{2+} ions over the possible positions, on change of the direction of the vector $\mathbf{l}_0$. We assume that the mobility of the Fe^{2+} ion drops discontinuously to zero at $T=T_c$, the "freezing" temperature of the process $Fe^{2+}\rightleftarrows Fe^{3+}$. Then for $T<T_c$, the distribution of Fe^{2+} ions over the specimen that existed at $T=T_c$ should be frozen in. Then if the crystal is cooled in a field $\mathbf{H}_0$, there arises in it a frozen-in 180° anisotropy with easy direction of $\mathbf{l}$ perpendicular to $\mathbf{H}_0$. Accordingly, the AFMR spectrum will have the form

$$(\nu/\gamma)^2=H(H+H_D)+H^2_{2\text{theor}}\cos 2(\varphi_l-\varphi_{l_0}), \qquad (12)$$

where

$$H^2_{2\text{theor}}=\frac{e_0^2NB}{2kT_c}\left(1+\frac{e_0}{8kT_c}\cos 6\varphi_{l_0}\right).$$

But if the crystal is cooled without a field, then for $T>T_c$ there are domains in it with different directions for $\mathbf{l}_0$; therefore for $T<T_c$, in each domain there is frozen in a 180° anisotropy with its own easy direction. The fact that in this case several AFMR lines, each with its own 180° anisotropy, are not observed experimentally indicates, apparently, that the dimensions of the domains are small. Then the AFMR spectrum is determined by the average of the anisotropy energy E_a over the whole specimen, which in this case is independent of the angle φ_l; consequently, neither the frozen-in anisotropy nor the isotropic and anisotropic gaps appear in the crystal ($H^2_{2\text{theor}}=0$, and $H^2_{\Delta\text{theor}}=H^2_{6\text{theor}}=0$).

Actually, of course, the mobility μ of the Fe^{2+} ion does not disappear discontinuously at $T=T_c$ but varies with temperature presumably as

$$\mu=\mu_0\exp(-\alpha T_c/T). \qquad (13)$$

The available experimental data are insufficient for determination of the function $\mu(T)$, because for $T\lesssim T_c$ it is impossible to calculate the anisotropy due to the impurity. A qualitative analysis enables us to state that on cooling of the specimen in a magnetic field at $T<T_c$, there should appear, along with a gap, also a frozen-in 180° anisotropy, and the corresponding constants in the AFMR spectrum change in the following manner: $H^2_{2\text{theor}}$ increases with lowering of the temperature; $H^2_{\Delta\text{theor}}$ and $H^2_{6\text{theor}}$, on the contrary, decrease to the same degree with respect to the values given by formulas (10) and (11). Such opposite behavior of $H^2_{2\text{theor}}$ on the one hand and of $H^2_{\Delta\text{theor}}$ and $H^2_{6\text{theor}}$ on the other is explained by the fact that the lower the temperature, the smaller the mobility μ and therefore, roughly speaking, the larger the number of Fe^{2+} ions that will be "frozen." It is these "frozen" ions that are responsible for formation of the frozen-in anisotropy; but on the other hand, they do not participate in the formation of the gaps H^2_Δ and H^2_6.

For comparison of these results with experiment, the values of $H^2_{\Delta\text{theor}}$ were calculated by formulas (10) and (11) for various values of the parameter e_0. If we exclude the regions $T\lesssim T_c$ and $T\gtrsim T_{\text{diss}}$, where formulas (10) and (11) give too large values of the gaps—in the first case because of decrease of the mobility μ, in the second because of decrease of the number of pairs N in consequence of dissociation—we can carry out a quantitative comparison over the range 20 to 100 K approximately.

The comparison showed (see Fig. 3) that for $e_0/k\sim 3$ K formula (10) describes the experiment well. It is natural that the theoretical curve, in the temperature interval indicated, should lie somewhat below the experimental, since there are other mechanisms, besides that considered, that make a contribution to H^2_Δ, for example the magnetostrictive, as in pure hematite.[14] As indication of this is the agreement of the values of H^2_Δ in $\alpha\text{-}Fe_2O_3$ and in $\alpha\text{-}Fe_2O_3+Sn^{4+}$ at $T=293$ K.

From consideration of Fig. 4 it is evident that the sharp rise of H^2_6 at low temperatures also agrees with the relation (11). Our value of the activation temperature of the electronic jump $Fe^{2+}\rightleftarrows Fe^{3+}$, $T_c\sim 20$ K, is close to those measured on other materials.[13,15] The quantitative agreement obtained between theory and experiment, with the reasonable value $e_0/k=3$ K for Fe^{2+} (this corresponds to an anisotropy field $H_a=2e_0/g\mu_BS\sim 10^4$ Oe), indicates that the mechanism considered actually operates and plays an important role in the formation of "frozen in" anisotropy and of an isotropic gap in $\alpha\text{-}Fe_2O_3+Sn^{4+}$. The latter statement has independent significance, since the antiferromagnetic crystals that have been investigated always have a certain quantity of impurities. It is therefore possible that the gap in the AFMR spectrum that is observed in certain materials, for example in $FeBO_3$,[16] and that increases with lowering of temperature, is of impurity character.

In conclusion, the authors take this opportunity to express their thanks to Academician A.S. Borovik-Romanov for his interest in the research and to V.I. Marchenko and A. V. Zalesskiĭ for useful discussions.

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Surface diffusion and interaction of adsorbed barium atoms on the (011) face of molybdenum

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The surface diffusion of barium adsorbed on the (011) face of molybdenum has been investigated in the region of submonolayer coverage. Plateau segments are observed in the diffusion distributions at adsorbed-atom concentrations at which ordered two-dimensional lattices of the type $c(6\times2)$ and $c(2\times2)$ are formed. The diffusion coefficient and diffusion activation energy change nonmonotonically with change of the degree of coverage of the surface by barium and have extremal values at the indicated concentrations. It is observed that in diffusion from a layer thicker than a monolayer, there is propagated along the surface not a dense monolayer (the unrolling-carpet mechanism) but a submonolayer phase $c(2\times2)$. The results are discussed on the basis of the data obtained previously on the features of interaction of adsorbed atoms (adatoms) and on phase transitions in submonolayer films of barium on Mo(011).

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INTRODUCTION

Studies of the atomic structure of adsorbed films, the kinetics of adsorption and desorption, and the influence of the films on the work function of the surface reveal an extremely complicated nature of the interaction of the particles adsorbed on the surface.[1]

A number of studies[2-9] show that study of surface diffusion on single-crystal substrates can also be an important source of information on the interaction of adsorbed atoms (adatoms). Up to the present time very few such studies have been carried out. This is due to difficulties in setting up the experiments, in which it is necessary to measure with high accuracy the distribution of the diffusing material on a surface which has a known atomic structure and a negligible number of defects. Such experiments are of course necessary also in order to shed light on the mechanisms of the diffusion processes themselves.

In the present work we have investigated the diffusion of barium on the (011) face of molybdenum. This system was chosen because detailed information has been obtained previously by various methods regarding the properties of barium films on this substrate (the atomic structure of the films and the phase transitions in them, and the concentration-dependence of the work function and heat of adsorption).[3] Preliminary results of the present work have been published elsewhere.[9]

METHOD

The experiments were carried out in glass apparatus under conditions of ultrahigh vacuum. The technique used[2] was based on recording the distribution of the work function φ over the substrate. With the aid of the known dependence $\varphi(n)$, where n is the concentration of adatoms, the transition is accomplished from φ to the concentration distribution. The work function was measured with an accuracy 0.02 eV by a contact-potential-difference method by means of an electron gun (Fig. 1) with a small exit aperture (~20 μm). To avoid spreading of the electron beam, the apparatus was placed in a longitudinal magnetic field H.

The system permitted the surface to be probed by the electron beam in two mutually perpendicular directions.