PECULIARITIES OF THE EXCITON-MAGNON INTERACTION IN ANTIFERROMAGNETIC CRYSTALS WITH THE PEROVSKITE STRUCTURE

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The optical absorption spectrum of the antiferromagnetic $RbMnF_3$ and $KMnF_3$ crystals possessing a perovskite structure is studied in the $^6A_{1g}(^6S) \rightarrow {}^4E_g(^4G)$ transition range in the Mn^{2+} ion. The measurements are carried out between 4.2 and 77°K. The effects of a strong magnetic field (up to 200 kOe) and of uniaxial deformations (up to 1000 kg/cm^2) on the spectrum are also investigated. Light absorption bands due to exciton-magnon transitions involving either one or two magnons are detected. The intensity of two-magnon optical transitions is found to be of the same order of magnitude as the intensity of one-magnon transitions. The most efficient in exciton-magnon transitions are spin waves with an energy $\nu_M = 56$ cm^{-1} (61 cm^{-1}) and a quasimomentum $k_M = \pi/2a$ corresponding to the edge of the magnetic Brillouin zone in $RbMnF_3$ ($KMnF_3$). The effect of a magnetic field on the structure of the optical spectrum can be qualitatively explained by magnetostriction in a strong field.

THE chief distinguishing feature of the structure of antiferromagnets of the perovskite type consists in the fact that the lattice parameter of the magnetic lattice is double the crystallographic lattice parameter.[1] This circumstance can, generally speaking, lead to peculiarities of the spin-wave spectrum and of the light absorption spectrum due to the exciton-magnon interaction.

The spin-wave spectrum of $RbMnF_3$ has been experimentally investigated with the aid of neutron scattering.[2] The results obtained were presented without account of the above-mentioned peculiarity of the magnetic structure. However, for the absorption of light by an antiferromagnetic crystal, it is essential to take into account the true periodicity of the magnetic structure, since selection rules which follow from the law of conservation of momentum are very important in this instance.

The optical absorption spectrum of crystals of manganese double fluorides ($MeMnF_3$, Me = Na, K, Rb, and Cs) has been investigated by Ferguson and co-workers,[3] Stevens,[4] and in more detail by us.[5,6] It was noted that the intense absorption of light is due to the lifting of the spin forbiddenness on account of the pair exchange interaction,[3,6] and also on account of the presence in $RbMnF_3$ and $KMnF_3$ of magnon satellites[5] analogous to those that have previously been observed in the spectrum of antiferromagnetic fluorides with the rutile structure.[7-10] At the same time, it follows from the theoretical work of Moriya[11] that the appearance of magnon satellites in the optical spectra of $RbMnF_3$ and $KMnF_3$ is unlikely, since the pair formed by the two nearest Mn^{2+} ions from the sublattices with opposite spins has a center of inversion.

All that has been said above induced us to undertake a detailed investigation of the fine structure of the optical absorption spectrum of $RbMnF_3$ and $KMnF_3$ crystals and the effect strong magnetic fields have on it in the region of sufficiently low temperatures ($T < T_N$, where T_N are the Néel temperatures which are 82 and 88°K for $RbMnF_3$ and $KMnF_3$ respectively).

EXPERIMENTAL METHODS

Absorption spectra of 0.2—5.5 mm single-crystal platelets[1)] were investigated. A DFS-13 diffraction spectrograph with a linear dispersion of 2 Å/mm and a resolving power of 144000 was used as the spectral device. The technique of low-temperature spectral and pulsed magneto-optic investigations has been described in detail previously.[12,13] Here we shall merely note that this technique allows one to carry out investigations in the broad spectral range from 7000 to 2500 Å at 4.2, 20, 4, and 77°K and intermediate

[1)]The single crystals for this investigation were prepared by S. V. Petrov (Institute of Physics Problems, USSR Academy of Sciences). We take the opportunity to express to him our sincere gratitude.

temperatures in magnetic fields of up to 200 kOe. Inasmuch as the structure of the investigated crystals is close to cubic,[1] all measurements were carried out in unpolarized light.

EXPERIMENTAL RESULTS

Detailed data on the frequencies and intensities of all the observed absorption bands in the $RbMnF_3$ and $KMnF_3$ spectra and a detailed analysis of the electron-vibrational structure of the spectra are presented in another paper.[6] In this paper, we will dwell only on those facts which are directly connected with the antiferromagnetism of the investigated crystals, and could possibly help in elucidating the peculiarities in their exciton-magnon interaction.

Let us consider the group of absorption bands identified with the $^6A_{1g}(^6S_{5/2}) \rightarrow {}^4E_g(^4G)$ transition in the Mn^{2+} ion. Even with account of the low symmetry of the ligand field and of the spin-orbit splitting of the $^4E_g(^4G)$ term, one cannot successfully explain the presence of so large a number of bands in the region of the C group of $RbMnF_3$ and $KMnF_3$. In the $RbMnF_3$ spectrum a number of bands is observed only when a sufficiently strong magnetic field ($\sim 10^5$ Oe) is turned on; these become stronger with further increase of the field. In the $KMnF_3$ spectrum, on the other hand, (for a sufficiently thick sample) some of these bands are also observed without a magnetic field. The dependence of the frequency of the absorption bands under consideration on the strength of the external magnetic field is given in Fig. 1.[2)]

It is possible that the dependence of the intensity on the field is not related to the antiferromagnetism of the investigated crystals, but is similar to the "enhancement" of bands observed in nonmagnetic crystals because of the mixing of various states in the Zeeman splitting of levels.[14]

The most appreciable changes were observed in the region of the group of absorption bands of $RbMnF_3$ near 25146 cm^{-1} (Fig. 1a). The structure of this group at 4.2°K and H = 0 is shown in Fig. 2 where one can readily see the 25145/25147 cm^{-1} doublet and the shorter-wavelength satellite at 25153 cm^{-1}. With increasing intensity of the magnetic field the interval between the doublet components increases and in a field H = 200 kOe it reaches 6 cm^{-1}. In addition, in a field H = 10^5 Oe

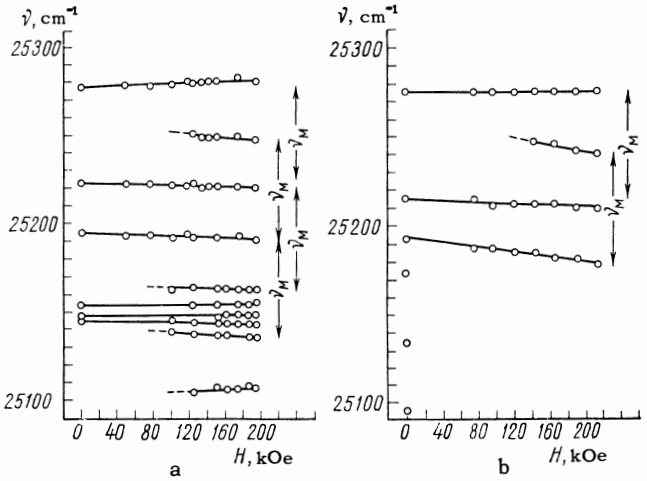

FIG. 1. Dependence of the frequencies of the absorption bands on the strength of the magnetic field (T = 20.4°K): a–$RbMnF_3$, b–$KMnF_3$. Bands which appear only in fields ~ 10^5 Oe are enhanced with increasing external magnetic fields.

there appear on the long and short-wavelength sides of the doublet additional "magnetic" bands whose intensity increases with increasing magnetic field; as a result a quartet of equally spaced bands is formed (with an interval of 6–8 cm^{-1}). The appearance of "magnetic" bands leads to the circumstance that for H > 100 kOe one encounters in the $RbMnF_3$ spectrum the interval $\Delta\nu = 56(\pm 1)$ cm^{-1} not once, but at least four times (Fig. 1a). The bands 25135, 25190, and 25246 cm^{-1} (H = 200 kOe) form a series in which the interval $\Delta\nu = 56$ cm^{-1} occurs twice. In the $KMnF_3$ spectrum one can also pick out a similar interval (61 cm^{-1}, Fig. 1b). We note immediately that the magnitudes of these frequency intervals are related to one another almost as the Néel temperatures of the compounds: $\Delta\nu^K/\Delta\nu^{Rb} = 61/56 = 1.09$, $T_N^K/T_N^{Rb} = 88/82 = 1.07$.

The shape of the satellite bands separated from the usual bands by an interval $\Delta\nu$ is noticeably asymmetrical (Fig. 3). The long-wave wing is more developed. The intensity of the satellite bands is comparable with the intensity of the usual

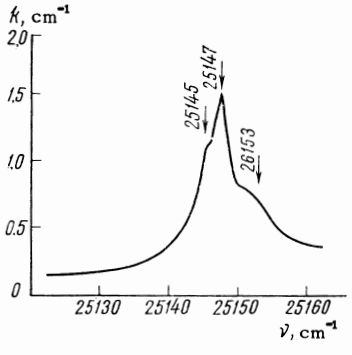

FIG. 2. The structure of the 25146 cm^{-1} band in the spectrum of $RbMnF_3$, T = 4.2°K.

2)Investigations of the Zeeman effect of $KMnF_3$ crystals of appreciable thickness were not carried out; this did not permit us to study the behavior of weak absorption bands in a magnetic field.

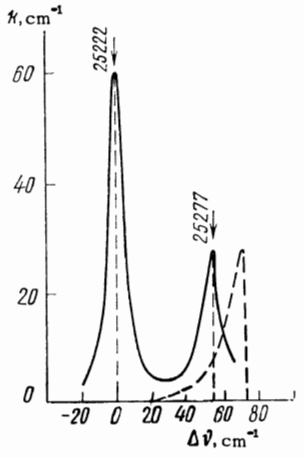

FIG. 3. Shape of the no-magnon and one-magnon bands in the spectrum of $RbMnF_3$, T = 20.4°K. The dashed curve is the calculated shape of the exciton-magnon light absorption band.

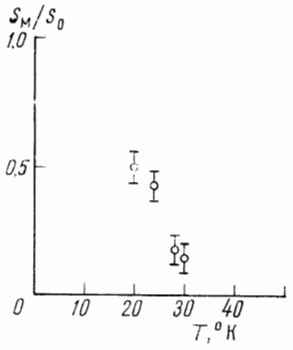

FIG. 4. Temperature dependence of the ratio of the integrated intensities of the exciton-magnon band ν = 25277 cm^{-1} and the no-magnon band ν = 25222 cm^{-1} in the spectrum of $RbMnF_3$.

bands. However, its temperature dependence, carefully measured for the 25277 cm^{-1} band as an example, is quite unusual: although the satellite band narrows sharply just as the main bands [5] on cooling below T_N, the value of the absorption coefficient at its maximum increases even more sharply. As a result the integrated intensity of the satellite band increases appreciably on cooling the sample, and is very weak at temperatures close to T_N. The integrated intensity of the usual electronic band ν = 25222 cm^{-1} [$^6A_{1g} \rightarrow {}^4E_g(^4G)$] does not change with temperature and is within experimental error equal at 77 and 4.2°K.

The temperature dependence of the ratio of the integrated intensities of the 25222 cm^{-1} and 25277 cm^{-1} bands is depicted in Fig. 4.

DISCUSSION

The temperature dependence of the frequency of the maxima of the satellite bands has been investigated in detail in the instance of the 25277-cm^{-1} $RbMnF_3$ and 25276-cm^{-1} $KMnF_3$ bands.[5] Their asymmetric shape and the decrease in their integrated intensity on heating give grounds for assuming that these bands are due to exciton-magnon transitions. For such transitions, when a photon produces an exciton and a magnon, the conservation laws are written as follows:

$$\mathbf{k}_{exc} + \mathbf{k} = \mathbf{k}_{phot} \approx 0, \quad (1)$$

$$h\nu_{phot} = E_0 + E_{kin} + h\nu, \quad (2)$$

where $\mathbf{k}_{exc}$, $\mathbf{k}_{phot}$, and $\mathbf{k}$ are the wave vectors of the exciton, photon, and magnon respectively; $h\nu_{phot}$ and $h\nu$ are the energies of the photon and magnon; E_0 is the energy for the production of an exciton, E_{kin} is its kinetic energy, $E_{kin} = \hbar^2 k_{exc}^2 / 2m^*$. Since the exciton bands connected with the excitation of 3d electrons are narrow ($m^* \gg 1$), the kinetic energy of the exciton E_{kin} can be neglected. Taking into account the conservation laws (1) and (2), the spectral distribution for the absorption coefficient in the region of the exciton-magnon transition is written in the following form:

$$\alpha_1(\nu) = 4\pi C_1 k^2 \left(\frac{d\nu}{dk}\right)^{-1} S_1(k). \quad (3)$$

Here $\nu = (h\nu_{phot} - E_0)/h$, $(C_1 S_1)$ is the exciton-magnon coupling parameter, and C_1 is a constant; as in the case of the spin-orbit mechanism,[7] we have also in the case of the exchange mechanism[11] of induction of exciton-magnon transitions

$$S_1^{1/2}(k) = \sum_{\delta_k} \sin(\delta_k k), \quad (4)$$

where δ_k is the projection of a vector connecting two nearest ions with opposite spins onto the $\mathbf{k}$ direction; in antiferromagnets with the perovskite structure (for example, $RbMnF_3$ and $KMnF_3$) δ_k = a is the parameter of the crystallochemical unit cell.

Making use of the expression for the energy of the spin waves,[2] (taking into account that the exchange integrals appearing in it $J_2 = J_3 = 0$, and neglecting the anisotropy field H_a)

$$h\nu(k) = 4SJ_1(9 - A^2)^{1/2}, \quad (5)$$

where S is the spin of the ion, J_1 is the exchange integral between nearest neighbors, and

$$A = \cos ak_x + \cos ak_y + \cos ak_z, \quad (6)$$

one can now readily calculate the shape of the exciton-magnon absorption band. The result is shown in Fig. 3; the dashed curve is calculated. This curve is similar to the experimental dependence of the absorption coefficient in the region of the satellite band, but is shifted towards higher energies. This discrepancy is due to the fact that the dispersion law of the spin-wave energy (5) was set down without allowance for the difference between the period of the magnetic structure (2a) and that of the crystallochemical structure (a).

The spin-wave spectrum of $RbMnF_3$ in Fig. 5, reconstructed from neutron scattering,[2] has been

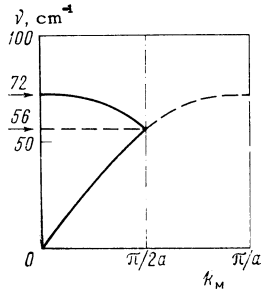

FIG. 5. Spin-wave spectrum in $RbMnF_3$ with account of the periodicity of the magnetic structure.

plotted with allowance for the periodicity of the magnetic structure. It is significant that at the edge of the magnetic Brillouin zone, for $k = \pi/a$, the energy of the spin wave is $\nu_M = 56\ cm^{-1}$. The shape of the exciton-magnon band, plotted in accordance with Eq. (3) with a dispersion law for spin waves which takes into account the periodicity of the magnetic structure, is analogous to the dashed curve of Fig. 3, but the maximum is at $\nu_M = 56\ cm^{-1}$. This is in excellent agreement with the interval $\Delta\nu = 56\ cm^{-1}$ picked out in the optical absorption spectrum of $RbMnF_3$. In $KMnF_3$ the interval $\Delta\nu$ should be somewhat larger, since its Néel temperature is higher; this is indeed observed experimentally.

As has been noted in the presentation of the experimental results (Fig. 1), the interval $\Delta\nu = 56\ cm^{-1}$ is encountered in the optical spectrum several times. Certain bands, for example at 25135 and 25246 cm^{-1}, are separated by an interval of 111 $cm^{-1} \approx 2\nu_M$. This circumstance compels us to assume that in the absorption of light of the investigated antiferromagnets processes are possible in which a single photon produces simultaneously an exciton and two magnons. Let us attempt to estimate the probability of the two-magnon mechanism. The conservation laws for this case can be written in the following form:

$$h\nu_{phot} = E_0 + E_{kin} + h\nu' + h\nu'', \tag{7}$$

$$\mathbf{k}_{phot} = \mathbf{k}_{exc} + \mathbf{k}' + \mathbf{k}''. \tag{8}$$

The interaction parameter of an exciton having a momentum $\mathbf{k}_{exc}$ with two magnons is the sum of the probabilities of its interaction with each possible pair of magnons with quasimomenta $\mathbf{k}'$ and $\mathbf{k}''$ satisfying the conservation law (8):

$$C_1^2 S_2(\mathbf{k}_{exc}) = \sum_{\mathbf{k}', \mathbf{k}''} S(\mathbf{k}', \mathbf{k}''). \tag{9}$$

A large number of pair combinations of $\mathbf{k}'$ and $\mathbf{k}''$ which satisfy the conservation law (8) is possible for a given $\mathbf{k}_{exc}$. The sets of these combinations differ little for excitons with various $\mathbf{k}_{exc}$ and therefore S_2 apparently depends weakly on k_{exc}[3)].

Owing to this we shall estimate the probability of the two-magnon absorption mechanism taking into account only the spectral dependence of the density of states in the spin-wave band and assuming S_2 to be constant. For simplicity (the estimates are only of a qualitative nature) we shall consider the dispersion law to be linear:

$$\nu = vk, \tag{10}$$

where v is the velocity of the spin wave. We introduce a dimensionless wave vector: $\kappa' = k'/k_{max}$ and $\kappa'' = k''/k_{max}$ where k_{max} is the value of the wave vector at the edge of the Brillouin zone. If we introduce the notation $\tilde{k} = (h\nu_{phot} - E_0)/vk_{max}$, then the coefficient of light absorption with the production of an exciton and two magnons is found as follows:

$$\alpha_2(\nu) = (4\pi C_1)^2 v^{-1} \int_0^1 \kappa'^2 d\kappa' \int_0^1 \kappa''^2 \delta(\kappa' + \kappa'' - \tilde{k}) d\kappa''. \tag{11}$$

In the same approximation (linear dispersion law, neglect of the dependence of S_1 on κ') the coefficient of light absorption with the production of an exciton and one magnon is

$$\alpha_1(\nu) = 4\pi C_1 \tilde{k}^2 / v. \tag{12}$$

Simple arguments indicate that

$$\alpha_2(\nu) \sim \tilde{k}^5, \quad \alpha_2(2\nu_M) \cong 2\pi C_1 \alpha_1(\nu_M). \tag{13}$$

The results of the simplified calculation attest to the fact that the intensity of the two-magnon transition is comparable with the intensity of the one-magnon transition if $C_1 \geq 0.15$. Allowance for the spectral dependence of the exciton-magnon pairing parameter should, of course, make the shape of the band more precise, but it will hardly change the qualitative conclusion concerning the considerable probability of a two-magnon process. It is thus possible that there is reason to assume that the 25246 cm^{-1} band of $RbMnF_3$ ($\nu = \nu_{00} + 2\nu_M$) is due to the simultaneous production of an exciton [$^6A_{1g} \rightarrow {}^4E_g({}^4G)$] and two magnons with an energy $\nu_M = 56\ cm^{-1}$ corresponding to the edge of the magnetic Brillouin zone ($k_{max} = \pi/2a$).

Let us finally consider the effect of an external magnetic field on the intensity and frequencies of light absorption bands in perovskite antiferromag-

[3)] Analogous arguments were employed in [15] where estimates were made of the probability of exciton annihilation with the production of a photon and two phonons.

nets. Speaking of intensities, one must above all note their large differences for various bands of the C group: the absorption coefficient at the maximum of the 25222 cm^{-1} bands of $RbMnF_3$ and of 25215 cm^{-1} in $KMnF_3$ approaches 50 cm^{-1}, and in the case of the remaining weak bands it is 0.5—15 cm^{-1}. Such a strong difference in the intensity of the bands attests to a difference in the nature of the transitions which give rise to these bands. The intense bands are apparently connected with electric-dipole transitions, and the weak bands—with magnetic-dipole transitions. It is important that both the spin-orbit [7] and exchange [11] mechanism of the exciton-magnon interaction transform a weak magnetic-dipole, purely-exciton transition into an electric-dipole, exciton-magnon transition. Indeed, as the experimental investigations of spectra of antiferromagnets with a rutile structure have shown,[7-10] the magnon satellites are much more intense (by 2—3 orders) than the pure exciton, no-magnon bands.

On the other hand, in the case of the $RbMnF_3$ and $KMnF_3$ investigated in this work the intensities of the pure exciton bands and of the magnon satellites are of the same order; the satellites are even somewhat weaker than the no-magnon bands (see, for example, Fig. 3). This circumstance does not contradict the symmetry considerations[11] from which it follows that the probability of the interaction of an exciton with short-wave magnons differs from zero, if only two of the closest ions from opposing magnetic sublattices make up a pair that is nonsymmetric with respect to the operation of inversion in the crystal. In crystals with the rutile structure this condition is certainly fulfilled, and in $RbMnF_3$ and $KMnF_3$ it is fulfilled to the extent to which the perovskite structure is disturbed. It is, therefore, not surprising that the intensity of the magnon satellites is small compared with the no-magnon bands. Here one should note again that with increasing external magnetic field strength, the intensity of some bands—magnon satellites—increases sharply, becoming even more intense than the no-magnon band. This circumstance apparently attests to the dependence of the exciton-magnon interaction constant C_1 on the magnetic field strength H.

In this connection one should attempt to explain the dependence of the splitting of the band in the region of 25146 cm^{-1} and of the intensity of a number of weak bands (including exciton-magnon lines) on the magnetic field. The magnetic field could hardly lead directly to splitting, since in cubic antiferromagnets with weak anisotropy the magnetic sublattices are oriented perpendicular to the external magnetic field, remaining equivalent, so that the sublattice degeneracy cannot be lifted. On the other hand, the Kramers degeneracy of electron levels in the magnetically ordered state has been lifted on account of the interaction with the exchange field H_E. The reason for the splitting can apparently only be the small deformation of the crystal due to the magnetostriction in a strong external magnetic field. The increase in in the intensity of weak absorption bands could possibly also be due to the magnetostrictive deformation of the crystal (in particular, the intensification of the magnon satellites is possible because of the violation of the symmetry of the pair with respect to the operation of inversion).

The hypothesis of the magnetostrictive mechanism of the effect of the external field on the optical spectrum of $RbMnF_3$ and $KMnF_3$ is confirmed by a number of facts. Indeed, the structure of $KMnF_3$ is more strongly distorted (differs more from the cubic O_h^1) than that of $RbMnF_3$.[1] In accordance with this, some of the bands which appear in $RbMnF_3$ only when a strong magnetic field is switched on are observed in $KMnF_3$ even with $H = 0$. The splitting of the 25146-cm^{-1} band in the $RbMnF_3$ spectrum is observed even without a magnetic field, but it is very small. The magnetic field merely increases this splitting. The doublet structure is also characteristic of other absorption bands of $RbMnF_3$.

In order to obtain a more convincing confirmation of the above hypothesis, we carried out an investigation of the direct effect of a directed deformation of a $RbMnF_3$ crystal on its optical spectrum. Since an appreciable uniaxial deformation can be obtained on compression of relatively thin single-crystal platelets in whose spectrum only intense absorption bands can be observed, all the results of the piezospectral measurements refer to the bands with $\nu = 25222$ cm^{-1} and $\nu = \nu_{00} + \nu_M = 25277$ cm^{-1}. No noticeable changes were observed in the region of the latter band, whereas the former splits on deformation into a doublet. Figure 6 shows the frequency dependence of the 25222-cm^{-1} absorption band on the deformation. With decreasing deformation the short-wave component becomes more intense, whereas the long-wave component becomes weaker and is altogether not observed at a pressure $P = 0$. The observed situation is very similar to the behavior of the 25146-cm^{-1} band in the magnetic field (see Fig. 1a).

Finally, we note that both the magneto-optical and piezospectral investigations carried out on

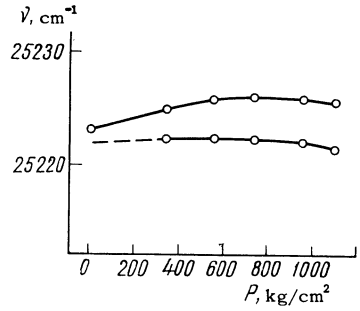

FIG. 6. Splitting of the $\nu = 25222$ cm^{-1} band in the spectrum of $RbMnF_3$ under the influence of a uniaxial deformation; T = 20.4°K.

several samples of arbitrary but certainly different orientation exhibited no appreciable anisotropy of these phenomena. The similarity of the spectral splitting in a magnetic field and in deformation, as well as the isotropy of both effects confirm rather convincingly the assumption concerning the magnetostrictive mechanism of the effect of a strong magnetic field on the light absorption spectrum in $RbMnF_3$ and $KMnF_3$ crystals.

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