Incommensurable Magnetic Surface Structures for MnO-Type Antiferromagnetic Insulators

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A calculation of the magnetic (001) surface structure of an antiferromagnetic insulator with the MnO spin arrangement is reported. The calculation is based on classical spins with Heisenberg interactions which are (a) between second neighbors throughout the bulk and surface, (b) between nearest-neighbor spins at the surface layer, and (c) between nearest-neighbor spins in the first and second layers. It is found that for a range of exchange parameters, *incommensurable* ground-state structures are obtained.

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The most common type of antiferromagnetic arrangement in the rock-salt-structure antiferromagnetic insulators is the one adopted by materials[1,2] such as NiO, CoO, MnO, and EuTe. In this structure *ferromagnetic* (111) planes are stacked antiferromagnetically, so that each magnetic ion is surrounded by six nearest neighbors of each spin, whereas all second nearest neighbors are aligned in antiparallel fashion. The observed arrangement is caused by the strong second-nearest-neighbor antiferromagnetic interaction J, which overwhelms the much smaller nearest-neighbor interaction. Various mechanisms can produce this ordering of strengths; one of the most quoted is the oxygen- or chalcogen-mediated antiferromagnetic superexchange[2,3]; that interaction utilizes the anion p orbitals, and is only effective for magnetic cations which are colinear with the anion. The superexchange interaction is therefore operational between second-nearest-neighbor spins, and vanishes for nearest neighbors: hence the observed strong second-nearest-neighbor exchange J.

In most of the materials mentioned above there is no magnetic rearrangement at the surface of the crystals[4]: The observed surface structure is the continuation up to the surface of the bulk arrangement. The interesting and unusual exception[5,6] is EuTe, where a magnetically rearranged (001) surface was observed by low-energy electron diffraction (LEED). The surface magnetic rearrangement is obviously related to the surface structural rearrangement and to the electronic surface structure, and can probably only appear in systems in which the changes in exchange interactions at the surface are of the same order of magnitude as the second-nearest-neighbor bulk antiferromagnetic Heisenberg coupling J. The surprise, however, is that the observed rearranged structure, at least at some temperatures, is *incommensurable* with both the lattice and the bulk magnetic structures. The k vector of the observed LEED pattern varies with temperature in a seemingly continuous way.

It is the purpose of this Letter to show that, if the surface atomic and electronic rearrangements, by whatever electronic mechanism, produce a sizeable (either ferro or antiferro) magnetic exchange K between nearest neighbors at the surface layer, and (either a ferro or an antiferro) magnetic exchange L between the surface layer and the one beneath it, it is possible, for some range in the values of K/J and L/J, to obtain magnetic surface structures which are incommensurable. It should be emphasized that the obtained ground state, one of *broken symmetry*, is obtained by a straightforward minimization of the total energy in a simple Heisenberg Hamiltonian: No other interactions are involved.

The calculation was performed for a semi-infinite system of *classical* spins of constant magnitude, with a (001) free surface, with second-neighbor antiferromagnetic exchange throughout the structure, and with nearest-neighbor interactions only at the surface two topmost layers:

$$E = J\sum_{(ij)} \mathbf{S}_i\cdot\mathbf{S}_j + K\sum_{\langle ij\rangle} \mathbf{S}_i\cdot\mathbf{S}_j + L\sum_{[ij]} \mathbf{S}_i\cdot\mathbf{S}_j, \qquad (1)$$

where $\mathbf{S}_i$ is a classical spin at site i, the parentheses designate second-nearest-neighbor pairs throughout the structure, the angle brackets indicate nearest-neighbor pairs *both* at the surface layer, and the square brackets symbolize nearest-neighbor pairs for one ion at the surface and the other in the layer immediately under it. The problem was treated as a simple minimization of the energy with respect to the spin orientations, subject to the constraint that in the bulk the spins are (arbitrarily) oriented along the z axis and that there is a single-domain structure (out of the possible eight {111} domain arrangements). In practice the calculation was carried out in the following way.

(a) All layers except the two closest to the surface were assumed to have, in all cases, the bulk structure.

(b) The surface was divided into square unit cells with four surface atoms in each; there were therefore eight atoms per unit cell in the two topmost layers.

(c) Initially all possible fully periodic arrangements [with the periodicity described in (b)] of the eight-atom unit cell were exhaustively examined, and the lowest-

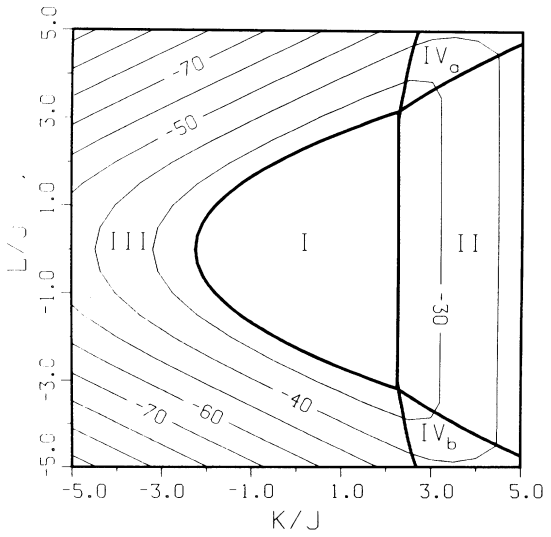

FIG. 1. Map in K/J-L/J parameter space of the *commensurable* structures of minimum energy. Region I is the unreconstructed, bulklike surface. In region II the various spins acquire an x-y component and tilt away from their original $\pm z$ orientation. In the limit $K/J \rightarrow \infty$ the surface is a perfect square antiferromagnet, with surface ions aligned in the x-y plane and with each spin surrounded by four spins of exactly the opposite orientation. Region III is similar, but with the surface spins tilting towards the perfect ferromagnetic arrangement in the x-y plane. Regions IV_a and IV_b correspond to more complicated spiral-type arrangements. The contours are the energies (in units of J) per unit cell of the eight spins in the two top layers.

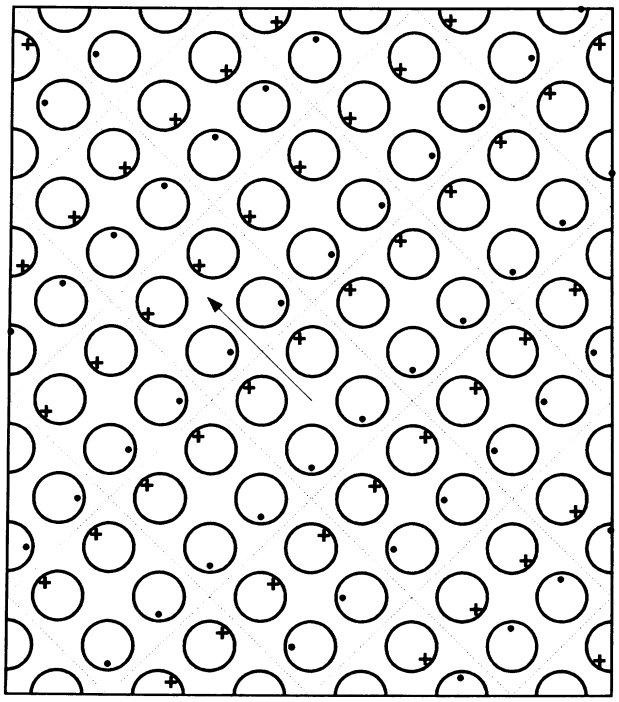

FIG. 2. The surface layer of an incommensurable structure corresponding to $K/J = L/J = 2.25$. The direction of the incommensurable k vector is indicated in the figure; the magnitude differs from that of the four-cell commensurable structure by about 2%. The spins are indicated in a stereographic projections, with dots pointing upwards, and crosses pointing downwards.

energy state thus determined; these states are labeled the *commensurable* states; the regions of stability of the various commensurable arrangements are shown in the K/J-L/J parameter space in Fig. 1. The region labeled I corresponds to an unreconstructed surface structure; in region II the various spins acquire an x-y component and tilt away from their original $\pm z$ orientation. In the limit $K/J \rightarrow \infty$ the surface is a perfect square antiferromagnet, with surface ions aligned in the x-y plane and with each spin surrounded by four spins of exactly the opposite orientation. Region III corresponds to a similar canting, but with the surface spins tilting towards the perfect ferromagnetic arrangement in the x-y plane. Regions IV_a and IV_b correspond to more complicated spiral-type arrangements. It should be mentioned that all these arrangements have Fourier components compatible with the four-surface-ion unit cell. The second layer is also rearranged, and is paramount in determining the lowest-energy structure, as can be inferred from the phase stability dependence on L/J.

(d) Starting with these lowest-energy commensurable structures, spin-wave excitation modes were determined and analyzed. It was found that, in some regions in parameter space, some spin-wave modes yielded negative energies,[7] a clear sign of instability of the assumed ground state. For those cases a complete minimization of the energy with the "frozen" soft mode, allowing for changes in amplitude and k vector was performed. The result is an *incommensurable* structure with, in some cases, a recognizable commensurable-state background, to which a frozen, incommensurable spin wave is superposed. A typical example is shown in Fig. 2. The new map of phase stability in parameter space is shown in Fig. 3. Regions i, ii, and iii, although with different boundaries, correspond exactly to the commensurable structures I, II, and III of Fig. 1. The shaded regions are the new incommensurable structures. All incommensurable structures, as found, have a single incommensurable k vector. The actual spin arrangements, however, have various structures and symmetries; the corresponding regions of stability in the K/J-L/J parameter space of Fig. 3 are labeled iv_a, iv_b, v_a and v_b. Ground states in the iv regions have an additional degeneracy (between x- and y-oriented k vectors) which does not exist in the v regions.

It is interesting to note that, as seen in Fig. 3, the stable structures along the $L/J = 0$ line are all commensurable, indicating that a nearest-neighbor coupling *to the bulk* is necessary in order to obtain incommensurable structures.

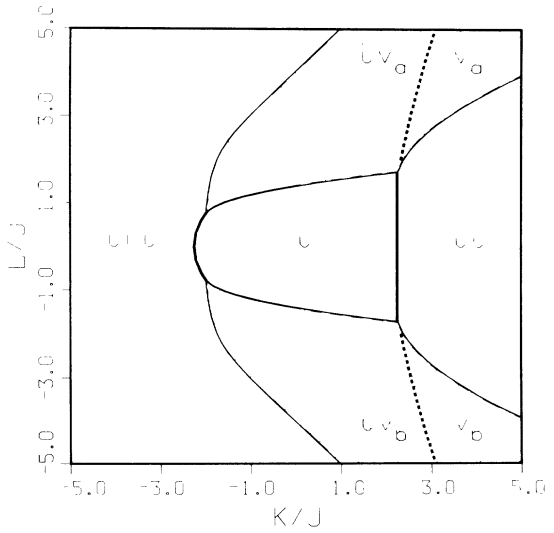

FIG. 3. Stability phase diagram, in K/J-L/J parameter space, of all examined structures. Regions i, ii, and iii are commensurable, and identical to the corresponding regions of Fig. 1. The shaded regions are the *incommensurable* structures. All incommensurable structures, as found, have a single k vector. The states labeled iv_a and iv_b have an extra degeneracy (between perpendicularly oriented k vectors) which does not exist in the v_a and v_b regions.

It is well known that competing interactions[8-10] may result in incommensurable structures. It is not surprising that incommensurability appears when the interactions are incommensurable with one another,[8] when both forces induce "frustration" throughout the system,[9] or when the exchange interactions are spin dependent.[10] In the case studied here the spin-independent interactions are commensurable with one another and with the lattice; they produce frustration only at the surface. The outcome is an incommensurable surface structure. The incommensurability does not arise from either "twisting" forces, or Fermi-surface related instabilities.[11-13]

The results reported here are similar to those found in the bulk of some alloys (the so-called axial next-nearest-neighbor Ising models[14,15]), but in that case, because of the metallic character, there was always the possibility that the effect, as observed experimentally, could be caused by Fermi-surface-type effects. In the particular case under study here, the effect only takes place in an *insulator* (i.e., there is no Fermi surface), and only at the surface,[16] where the competition between the disparate forces takes place.

It should be emphasized that the present calculation, although not complete in the sense that it has not examined *all* possible structures, guarantees the existence of incommensurable ground-state structures. Some structure not examined here could in fact have an energy lower then those reported. However, since all commensurable structures were examined and calculated, and for some parameters one incommensurable structure was obtained with energy lower than those of the commensurable phases, the ground state must, by necessity, be incommensurable for those values of the parameters.

No attempt has been made to fit the results of this calculation to the actual experiments on EuTe. Neither the experimental information available is sufficient, nor the (probably quantitatively important) quantum-mechanical aspects of the Eu spins ($S = \frac{5}{2}$) were included in the calculation. It has been demonstrated, however, that incommensurable surface structures are possible, and are most likely caused by the competing interactions between bulk and surface exchange parameters.

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